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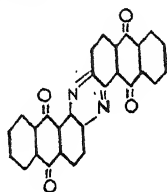


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LIST OF ERRATA TO VOL. XXXVII, 1941.

Page 69: Formula VIII should read



- „ 299: Equation (3), substitute $m(m + 1)$ for $m(m - 1)$.
- „ 300: Bottom line „ $20 - p'r_e$ for $20 \cdot p'r_e$.
- „ 301: Equation (6) „ $T = kn^{\frac{5}{3}} V^{-\frac{2}{3}}$ for $T = kn^{\frac{5}{3}} V^{-\frac{2}{3}}$.
- Equation (9) „ $2kmn^{\frac{5}{3}}$ for $2kmn^{\frac{5}{3}}$.
- (right-hand numerator)
- „ 302: Line 3 „ $m = 6$ for $m \times 6$.
- „ 7, delete "only".
- „ 512: Line 1. After first F insert comma and space.
- „ 515: At ends of lines 8 and 9 transpose "i" and "1."
- Fig. 2. Curve A is in top left corner.
- „ 518: For "Fig. 1a" read "Fig. 1b."
- „ 519: In first formula for "v" and "w" read "V" and "W" respectively.
- For "Fig. 1b" read "Fig 1a."
- In footnote *. For "p. 2" read "p. 509."
- „ 521: Line 2. For "t" read "i."
- „ 548: Line 9. For "Card" read "complete."



STUDIES OF THE MOLECULAR FORCES INVOLVED IN SURFACE FORMATION. I. THE SURFACE ENERGIES OF PURE LIQUIDS.

BY J. W. BELTON AND M. G. EVANS.

Received 4th October, 1940.

The advances which have been made in the last few years in the theory of the liquid state enable one to discuss with some certainty from a statistical point of view the thermodynamic functions of liquid-vapour phase equilibria. In this communication we propose to calculate the energy and entropy changes accompanying the formation of a liquid surface in terms of the intermolecular forces and the configurational behaviour of the molecules of the liquid and to show that the simple model employed in these calculations leads also to reasonable values of the latent heat of vaporisation and the vapour pressure. Such calculations of the total energy of a liquid have been made by Laplace (1806) and Gauss (1830) and Rayleigh (1890), and by many other writers.¹ More recently the energy of surface formation has been discussed in general terms by Harkins, Davies and Clark,² and attention has been directed to the chemical nature of the surface molecules by Langmuir³ and by Harkins. The expressions obtained for the total energy and for the surface energy of a liquid include a function $\epsilon(r)$ where r is the molecular separation, so that the complete calculation requires a knowledge of the attractive force between molecules. Bakker, for example, assumed this force to be an inverse exponential function of the distance. Attempts to calculate the total surface energy of liquids from the attractive forces between molecules have been made by Margenau,⁴ Bradley⁵ and by Kassel and Muskat,⁶ who showed that the surface tensions of liquefied permanent gases may be accounted for in terms of polarisation forces. More recently Fowler⁷ has calculated the parachors of certain liquids, and thus implicitly their surface tension, by using the methods of Laplace and Rayleigh modified by the introduction of a neighbour distribution function, and assuming a law of force

$$\epsilon(r) = \lambda r^{-9} - \mu r^{-6}.$$

It should be observed that the boundary between a liquid and its vapour is of the order of one or two molecules thick, and consequently the dividing surface between the phases may be assumed sharp: calculations based on a gradual transition from one plane to the other are necessarily erroneous.

¹ Gyanant *Handbuch der Physik*, 1927, Bd. VII, 343; Bakker, Wien-Harms, *Handbuch der Experimental Physik*, 1928, Bd. VI.

² Harkins, Davies and Clark, *J. Amer. Chem. Soc.*, 1917, 39, 541.

³ Langmuir, *ibid.*, 1848.

⁴ Morgenau, *Physic. Rev.*, 1931, 38, 365.

⁵ Bradley, *Phil. Mag.*, 1931, 11, 846.

⁶ Kassel and Muskat, *Physic. Rev.*, 1932, 40, 627.

⁷ Fowler, *Physica*, 1938, 5, 39.

The Thermodynamic Functions for the Liquid, the Surface, and the Vapour Phases.

The free surface energy is to be identified with a free energy accompanying the formation of a surface of unit area. This is the difference in free energy between a plane of unit area in the bulk of the liquid and one of unit area in the surface. The extent of the surface phase normal to the surface is taken over that region where the potential energies and configurational behaviour of the molecules are different from the potential energy and configurational behaviour in the bulk of the liquid. If the length of the co-ordinate normal to the surface over which molecules have different potential energies and configurational properties from molecules in the bulk is δ then in defining the free energy change accompanying surface formation a lamina of liquid in the bulk of the same thickness δ must be chosen as standard. In the cases we deal with here we shall show that δ is very clearly one molecular diameter. This, however, will not be general.

If we can define explicitly the partition functions for molecules in the bulk and in the surface of a liquid then it will be possible to calculate the thermodynamic properties of a surface in terms of intermolecular forces and molecular dimensions.

The partition function for a liquid of N_s molecules in which each molecule moves in identical potential energy fields (*i.e.*, changes in the potential energy fields arising from the discontinuity at the surfaces are neglected) can be written

$$f^{N_s} = J(T)^{N_s} B(T)$$

$J(T)$ is the partition function for those states of motion of the molecules which are independent of the configuration of molecules in the liquid. These states may include electronic, vibrational and rotational. $B(T)$ is the partition function for the translational motion of the molecules and will be a function of the configuration of the whole liquid.

The most convenient model of a liquid for this discussion is that of the quasi-crystalline structure in which each molecule of the liquid can be regarded as an isotropic three-dimensional harmonic oscillator of characteristic frequency ν . On the basis of this model the partition function for a liquid can be written

$$f^{N_s} = J(T)^{N_s} \phi(T)^{N_s} \exp \left(-\frac{N_s X_0}{kT} \right).$$

Here X_0 is the potential energy of a molecule at zero displacement from the "lattice point" and $\phi(T)$ is the partition function for the vibrational states of the molecule about this "lattice point." The thermodynamic functions of the liquid are given by the Helmholtz free energy or work function F ,

$$F = -N_s kT \left(\ln J(T) \phi(T) - \frac{X_0}{kT} \right) \quad (1)$$

the total energy E ,

$$E = -N_s kT^2 \frac{\partial}{\partial T} \ln J(T) \phi(T) + N_s X_0 + N_s T \frac{\partial X_0}{\partial T} \quad (2)$$

the entropy S ,

$$S = N_s k \left(\ln J(T) \phi(T) + T \frac{\partial}{\partial T} \ln J(T) \phi(T) - \frac{1}{k} \frac{\partial X_0}{\partial T} \right) \quad (3)$$

Now let us consider the behaviour of N_s molecules in the surface layer. If the surface layer is homogeneous, that is, if the molecules in the surface layer are all moving in potential energy fields which, while being different from the potential energy field for molecules in the bulk are identical for all molecules in the surface, then the partition function for the surface of N_s molecules is

$$f_s^{N_s} = J_s(T)^{N_s} \phi_s(T)^{N_s} \exp \left(-\frac{N_s \chi_s}{kT} \right)$$

where the subscripts s indicate quantities characteristic of the molecules in the surface layer. The postulate of homogeneity of the surface layer given above virtually restricts the surface layer to one of unimolecular dimensions. If, on the other hand, the surface layer is not homogeneous the partition function will be

$$f_s^{N_s} = \prod J_s^{n_1}(T) \phi_s^{n_1}(T) J_s^{n_2}(T) \phi_s^{n_2}(T) \dots \exp \left(-\frac{n_1 \chi_{s,1}}{kT} - \frac{n_2 \chi_{s,2}}{kT} - \dots \right)$$

the continued product being taken over $n_1, n_2, n_3 \dots n_n$ which are the numbers of molecules in the different layers of the surface phase and $n_1 + n_2 + \dots + n_n = N_s$. We will, however, restrict ourselves to the case of homogeneity, that is to a unimolecular surface layer.

The corresponding thermodynamic functions for the surface layer are given by

$$F_s = -N_s kT \left(\ln J_s(T) \phi_s(T) - \frac{\chi_s}{kT} \right) \quad (4)$$

$$E_s = -N_s kT^2 \frac{\partial}{\partial T} \ln J_s(T) \phi_s(T) + N_s \chi_s + N_s T \frac{\partial \chi_s}{\partial T} \quad (5)$$

$$S_s = N_s k \left(\ln J_s(T) \phi_s(T) + T \frac{\partial}{\partial T} \ln J_s(T) \phi_s(T) - \frac{1}{k} \frac{\partial \chi_s}{\partial T} \right) \quad (6)$$

and the changes in these functions accompanying the formation of a surface are

$$\Delta F = F_s - F = -N_s kT \left(\ln \frac{J_s(T) \phi_s(T)}{J(T) \phi(T)} - \frac{\chi_s - \chi_0}{kT} \right) \quad (7)$$

$$\Delta E = E_s - E = -N_s kT \left(T \frac{\partial}{\partial T} \ln \frac{J_s(T) \phi_s(T)}{J(T) \phi(T)} - \frac{\chi_s - \chi_0}{kT} - \frac{1}{k} \frac{\partial}{\partial T} (\chi_s - \chi_0) \right) \quad (8)$$

$$\Delta S = S_s - S = N_s k \left(\ln \frac{J_s(T) \phi_s(T)}{J(T) \phi(T)} + \frac{\partial}{\partial T} \ln \frac{J_s(T) \phi_s(T)}{J(T) \phi(T)} - \frac{1}{kT} \frac{\partial}{\partial T} (\chi_s - \chi_0) \right) \quad (9)$$

The above expressions relate to the thermodynamics of the formation of a surface containing N_s molecules in the surface layer from N_s molecules in the bulk of the liquid, and as we shall see later are simply related to the characteristics of the molal surface energy. The usual expression for surface energy refers to unit surface area and the partition function for the formation of unit surface area is

$$\frac{f_s^{1/\sigma_s}}{f^{1/\sigma}} = \frac{(J_s(T) \phi_s(T))^{1/\sigma_s}}{(J(T) \phi(T))^{1/\sigma}} \exp \left(-\frac{\frac{1}{\sigma_s} \chi_s}{kT} - \frac{\frac{1}{\sigma} \chi_0}{kT} \right)$$

where σ_s is the effective area occupied by one molecule in the surface and σ the effective area occupied by one molecule in the imaginary plane in the bulk of the liquid.

If the packing of the molecules is identical in the bulk and in the surface phase then σ and σ_s are equal. Now, however, the number of molecules, *i.e.*, $1/\sigma$ involved is not independent of temperature and hence the thermodynamic quantities have the following forms :

$$\Delta F = -\frac{kT}{\sigma} \left(\ln \frac{J_s(T)\phi_s(T)}{J(T)\phi(T)} - \frac{\chi_s - \chi_o}{kT} \right) \quad (10)$$

$$\Delta E = -\frac{kT}{\sigma} \left(T \frac{\partial}{\partial T} \ln \frac{J_s(T)\phi_s(T)}{J(T)\phi(T)} - \frac{\chi_s - \chi_o}{kT} - \frac{1}{k} \frac{\partial}{\partial T} (\chi_s - \chi_o) - \frac{T}{\sigma} \frac{\partial \sigma}{\partial T} \ln \frac{J_s(T)\phi_s(T)}{J(T)\phi(T)} \right) \quad (11)$$

$$\Delta S = \frac{k}{\sigma} \left(\ln \frac{J_s(T)\phi_s(T)}{J(T)\phi(T)} + T \frac{\partial}{\partial T} \ln \frac{J_s(T)\phi_s(T)}{J(T)\phi(T)} - \frac{1}{k} \frac{\partial}{\partial T} (\chi_s - \chi_o) - \frac{T}{\sigma} \frac{\partial \sigma}{\partial T} \ln \frac{J_s(T)\phi_s(T)}{J(T)\phi(T)} \right) \quad (12)$$

The latent heat of vaporisation and the vapour pressure of a liquid can be expressed in terms of the method outlined above. The expressions for the thermodynamic functions of the gas phase are :—

$$F = -NkT \ln J_g(T)\phi_g(T) \quad (13)$$

$$E = -NkT^2 \frac{\partial}{\partial T} \ln J_g(T)\phi_g(T) \quad (14)$$

$$\text{and} \quad S = Nk \left(\ln J_g(T)\phi_g(T) + T \frac{\partial}{\partial T} \ln J_g(T)\phi_g(T) \right) \quad (15)$$

Hence the free energy, total energy and entropy changes accompanying the change of N molecules from the liquid to the vapour state are :

$$\Delta F = -NkT \left(\ln \frac{J_g(T)\phi_g(T)}{J(T)\phi(T)} - \frac{\chi_o}{kT} \right) \quad (16)$$

$$\Delta E = -NkT^2 \frac{\partial}{\partial T} \ln \frac{J_g(T)\phi_g(T)}{J(T)\phi(T)} + N\chi_o - NT \frac{\partial \chi_o}{\partial T} \quad (17)$$

$$\Delta S = Nk \left(\ln \frac{J_g(T)\phi_g(T)}{J(T)\phi(T)} + T \frac{\partial}{\partial T} \ln \frac{J_g(T)\phi_g(T)}{J(T)\phi(T)} - \frac{1}{k} \frac{\partial \chi_o}{\partial T} \right) \quad (18)$$

In liquids of monatomic substances and at higher temperatures in liquids of more complex molecules the rotational and vibrational states of the molecules will be identical with those in the gas phase and hence $J_g(T)$ will be equivalent to $J(T)$.

In the previous discussion we have used the quasi-lattice structure of a liquid and have associated the partition function $\phi(T)$ with the vibrational states of the molecule about this lattice point. In the gas phase the molecules are not restricted in their movements in this way and are free to move in the whole free space available to this gas. For the purpose of computing vapour pressures and latent heats, however, it is more convenient to translate this partition function into one representing the translational behaviour of the molecules in an available free volume.

Using this conception the above thermodynamic functions reduce to

$$\Delta F = -NkT \left(\ln \frac{V_g}{eV_1} \left(\frac{m_g}{m_l} \right)^{\frac{3}{2}} - \frac{\chi_0}{kT} \right) \quad (19)$$

$$\Delta E = -NkT^2 \frac{\partial}{\partial T} \ln \frac{V_g}{eV_1} + N\chi_0 - NT \frac{\partial \chi_0}{\partial T} \quad (20)$$

$$\Delta S = Nk \left(\ln \frac{V_g}{eV_1} \left(\frac{m_g}{m_l} \right)^{\frac{3}{2}} + T \frac{\partial}{\partial T} \ln \frac{V_g}{eV_1} - \frac{1}{k} \frac{\partial \chi_0}{\partial T} \right) \quad (21)$$

Where V_g is the volume of N molecules in the gas phase under the standard conditions of 1 atmosphere pressure and temperature T and V_1 the free volume available to the molecules in the liquid.

The latent heat of vaporisation λ is related to the energy change ΔE by $\lambda = E + NkT - PV_1$, where in general the term PV_1 is a negligible quantity compared with ΔE and NkT , since V_1 is the volume of 1 mole of liquid.

The vapour pressure is given by

$$\ln p = \frac{N\chi_0}{RT} + \ln \frac{V_g}{eV_1} \left(\frac{m_g}{m_l} \right)^{\frac{3}{2}} \quad (22)$$

or separating out the temperature dependent part of χ_0 by writing

$$\chi_0 = \chi_0^0 + \int \frac{\partial \chi}{\partial T} dT$$

$$\ln p = \frac{N\chi_0^0}{RT} + \frac{1}{RT} \int \frac{\partial \chi}{\partial T} dT + \ln \frac{V_g}{eV_1} \left(\frac{m_g}{m_l} \right)^{\frac{3}{2}} \quad (23)$$

Changes in the Potential Energy of a Molecule on going into the Surface Layer.

In this communication we will restrict our discussion to those cases in which the attractive forces acting between molecules are additive and can be represented by a function of the distance only between the molecules, that is the molecules considered are spherical and the potential energy between two molecules is independent of their angular orientations.

If we consider the liquid as a "continuum" of attracting centres of ρ per unit volume, we can then write the potential energy change in bringing a molecule into the surface as

$$\chi_s - \chi_0 = \frac{\rho}{2} \int_a^\infty \frac{\mu}{x^6} 2\pi x^2 dx \quad (24)$$

where $2\pi x^2 dx$ is the number of molecules in a hemispherical shell, and the integration is made over all such shells from the distance of closest approach between two molecules and infinity. This leads to

$$\chi_s - \chi_0 = \frac{\pi \rho \mu}{24 r^3} \quad (25)$$

as the energy change per molecule, where r is the radius of a molecule. The expression for the number of molecules ρ per unit volume depends upon the geometric arrangement of the molecules in the bulk of the liquid.

The calculation of the molecular radius from the density of the liquid will depend on the type of packing and in general $r^3 = \gamma V/8$, where

V is the molecular volume and γ is a constant depending on the packing. We have used values of γ 1.27 and 1.47 for the cubical and hexagonal packings respectively.

The energy change accompanying the formation of unit area of surface is

$$\frac{\chi_s - \chi_0}{\sigma_s} = \frac{3\mu}{125r^6\sigma_s} \text{ for cubical packing, and } \quad (26)$$

$$\frac{\chi_s - \chi_0}{\sigma_s} = \frac{\mu}{48r^6\sigma_s} \text{ for hexagonal packing } \quad (27)$$

Since the potential energy function $\epsilon(r)$ decreases according to a high power of the inverse distance, we might assume that only the first shell of neighbouring molecules contributes to the potential energy of any given molecule X .

Fig. 1 gives a representation of a cross-section through a liquid in which the molecules have (a) close packing and (b) cubical packing.

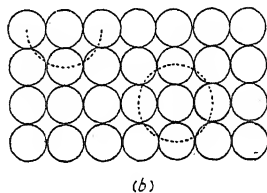
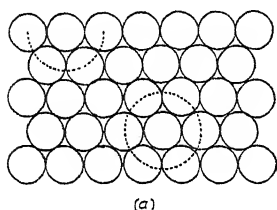


FIG. 1.

Consider molecule X in these patterns for the close packed structure, when molecule X is in the bulk of the liquid this molecule is surrounded by 12 molecules and by nine molecules when X is in the surface. For the cubical packed structure a molecule in the bulk is surrounded by six molecules when in the bulk and by five molecules when in the surface of the liquid.

The potential energy change corresponding to $(n_B - n_s)$ intermolecular contacts broken in going from the bulk of the liquid to the surface is $(n_B - n_s)\epsilon(r)$ where n_B and n_s are the co-ordination numbers for molecules in the bulk and in the surface respectively, and $\epsilon(r)$ is the potential energy of a pair of molecules at a separation r . But of the contacts broken one half are re-formed by the mutual interactions of molecules, and thus the net change in potential energy accompanying this process is

$$\frac{(n_B - n_s)}{2} \epsilon(r).$$

The change of potential energy in bringing a molecule of the close packed liquid into the surface is $\Delta\epsilon = \frac{3}{2}\epsilon(r)$.

Using the London expression for the potential energy between two molecules under the influence of dispersion forces, *i.e.*,

$$\epsilon(r) = \frac{3\alpha^2 h\nu}{4x^6} = \frac{\mu}{x^6} \quad (28)$$

where α is the polarisability of the molecule, $h\nu$ a characteristic resonance energy closely related to the ionisation potential, and x the distance between the centres, the change in potential energy becomes

$$\chi_s - \chi_0 = \frac{3}{128} \frac{\mu}{r^6} \quad (29)$$

where r is the radius of a molecule of the liquid. This is the energy per molecule. The energy per unit area of surface will be

$$\frac{\chi_s - \chi_0}{\sigma_s} = \frac{3\mu}{128r^6\sigma_s} \quad (30)$$

where σ_s is the area occupied by the molecule in the surface of the liquid. Throughout the subsequent calculations we have used the value of $(\chi_s - \chi_0)/\sigma_s$ given by equation (27).

The Value of σ_s .

As we have seen in the previous section the thermodynamic functions depend upon σ_s and σ where σ is the area available to a molecule in an imaginary plane in the bulk of the liquid. We have assumed σ_s and σ to be identical, that is, we have assumed that the packing is the same in the bulk and in the surface of the liquid. The value given to σ_s will, of course, depend upon the type of packing in the surface and we have chosen the extreme cases of σ_s given by πr^2 and $4r^2$ respectively, where $r = a/2$, a being the mean distance between two molecules of the liquid at any temperature.

We consider that the value $\sigma_s = \pi r^2$ is in general a better approximation to the area available per molecule than is $\sigma_s = 4r^2$.

Introducing these values into equations (26) and (27) for cubical and hexagonal packing respectively, we have for the energy change accompanying the formation of a surface of unit area

$$\frac{\chi_s - \chi_0}{\sigma_s} = \frac{3\mu}{500r^8} \quad (31)$$

and

$$\frac{\chi_s - \chi_0}{\sigma_s} = \frac{\mu}{48\pi r^8} \quad (32)$$

Let us now consider in detail the magnitudes of the quantities entering into equation (10) for the free energy change accompanying the formation of a surface of unit area. The value of ΔF is made up of two terms, one $(\chi_s - \chi_0)/\sigma_s$, the calculation of which we have discussed above, and

$$-\frac{kT}{\sigma_s} \ln \frac{J_s(T)\phi_s(T)}{J(T)\phi(T)}.$$

If we are considering liquids of monatomic molecules then the partition functions $J_s(T)$ and $J(T)$ for the rotational states do not appear, if we assume that in the cases of simple diatomic molecules containing no especially polar groups the rotational states of the molecule are identical in the surface and in the bulk of the liquid $J_s(T) = J(T)$, and in both these cases only the translational partition function $\phi_s(T)$ and $\phi(T)$ are left.

$\phi_s(T)$ and $\phi(T)$ will be in general different because even in the simplest cases and temperatures not in the neighbourhood of the critical temperature the formation of a surface of necessity introduces anisotropy into the three-dimensional oscillations of a molecule in the liquid. This anisotropy arises in the following way: in the bulk of the liquid a molecule is flanked by two neighbouring molecules for each dimension of oscillation, whereas in the surface for the oscillation in the dimension normal to the surface the molecule is vibrating in a potential field set

up by only one neighbouring molecule. The effect of this change of configuration on the potential field can be seen from Figs. 2*a* and *b*,

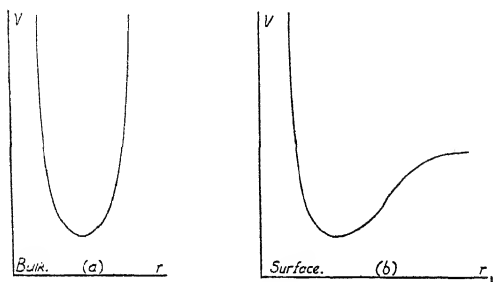


FIG. 2.

for whereas in the bulk of the liquid the molecule is moving against the repulsion forces set up by the flanking molecules, in the surface a molecule moving in the positive direction normal to the surface is moving against the softer attractive forces.

As a first approximation we may neglect consideration of this term

$\frac{kT}{\sigma} \ln \frac{\phi_s(T)}{\phi(T)}$ and calculate the contribution of $(\chi_s - \chi_0)/\sigma$ to the free energy change of surface formation. Reference to equation (12) for the entropy change accompanying surface formation, shows that to this approximation the entropy change is given by the temperature variation of $(\chi_s - \chi_0)$. It is important to emphasise that χ_s and χ_0 are both temperature dependent quantities, because, as we have pointed out, the value of r occurring in equations (3) and (4) is equal to $a/2$, where a is the effective difference between molecules and is related to the density, d , of the liquid by

$$\frac{a}{2} = \left(\frac{3M}{4\pi Nd} \right)^{\frac{1}{3}}$$

where M is the molecular weight of the substance. Fig. 3 shows potential energy curves at different temperatures for motion of a molecule along one dimension when it is flanked by two neighbours. We should

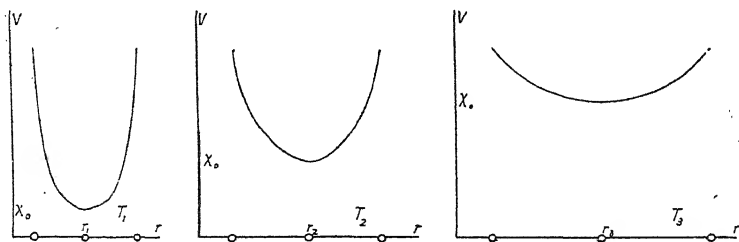


FIG. 3.

expect therefore that calculations of $(\chi_s - \chi_0)/\sigma$ at various temperatures should lead not only to reasonable values of the magnitude of the surface tension, but moreover, the temperature dependence should correspond fairly closely to that of the surface tension, if our assumption about the magnitude of $\phi_s(T)/\phi(T)$ is correct.

Table I gives the values of μ , the density d (at various temperatures), and the values of r obtained from the densities which are required for the calculation of $(\chi_s - \chi_0)$ in terms of the quantities in equation (27). Table II compares the calculated and observed values of the surface tension at different temperatures for a number of simple liquids. Fig. 4 shows the correspondence obtained graphically.

TABLE I.

Liquid.	μ .	T .	d .	r .
Helium	1.23×10^{-60}	1.4	0.1456	1.932
		2.3	0.1463	1.923
		3.1	0.1404	1.954
		3.9	0.1279	2.013
		4.2	0.1222	2.047
		2.21	0.1469	1.923
		2.28	0.1466	1.923
		2.47	0.1457	1.932
		3.21	0.1395	1.955
		3.81	0.1311	1.999
		4.13	0.1255	2.030
		85.0	1.4169	1.947
		90.0	1.3845	1.962
Argon	55.17×10^{-60}	25.08	1.238	1.626
Neon	4.66×10^{-60}	26.06	1.222	1.634
		27.06	1.204	1.639
		30.04	1.150	1.662
		33.00	1.088	1.695
Hydrogen	13.2×10^{-60}	14.6	0.07655	1.900
		16.1	0.07705	1.912
		17.9	0.07325	1.928
		18.7	0.07245	1.935
		20.4	0.07080	1.961
		70.0	1.2393	1.892
		75.0	1.2104	1.907
Oxygen	43.25×10^{-60}	80.0	1.1911	1.916
		85.0	1.1671	1.931
		90.0	1.1431	1.944
		20.0	0.8446	2.053
		75.0	0.8217	2.070
Nitrogen	61.4×10^{-60}	80.0	0.7988	2.090
		85.0	0.7759	2.108
		90.0	0.7530	2.137
		213	1.6167	2.258
		218	1.6055	2.262
Chlorine	458×10^{-60}	223	1.5945	2.269
		228	1.5830	2.274
		233	1.5720	2.278
		238	1.5589	2.284
		243	1.5485	2.291
		273	1.4678	2.331
		283	1.4380	2.347
		293	1.408	2.364
		303	1.377	2.376
		313	1.344	2.401
		323	1.310	2.421
Carbon monoxide . .	67.4×10^{-60}	70.0	0.8474	2.064
		75.0	0.8264	2.072
		80.0	0.8054	2.089
		85.0	0.7844	2.108

From these results the following points emerge:—

(1) The correspondence between the observed and calculated values is in most cases fairly close: this is especially true at the lower temperatures where the contribution of the term $\frac{kT}{\sigma} \ln \frac{\phi_s(T)}{\phi(T)}$ is smallest.

(2) There is a much larger deviation between the calculated and

observed temperature dependence of the surface tension (see Table III) : this discrepancy must be attributed to the influence of the term

$$\frac{kT}{\sigma} \ln \frac{\phi_s(T)}{\phi(T)}$$

which will become increasingly important as the temperature increases.

TABLE II.

Liquid.	T.	γ (calc.).		γ (observed).
		$A = 4\pi^2.$	$A = \pi r^2.$	
Helium	1.4	0.278	0.414	0.356
	2.3	0.289	0.428	0.318
	3.1	0.264	0.391	0.226
	3.9	0.197	0.290	0.133
	4.2	0.178	0.263	0.100
	2.21	0.291	0.430	0.326
	2.28	0.291	0.430	0.320
	2.47	0.284	0.421	0.300
	3.21	0.259	0.384	0.214
	3.81	0.215	0.318	0.144
	4.13	0.191	0.282	0.107
	85.00	12.0	17.8	13.2
Argon	90.00	11.4	16.7	11.9
Neon	25.08	4.36	6.45	5.47
	26.06	4.16	6.16	5.14
	27.06	4.03	5.97	5.76
	30.04	3.56	5.26	3.71
	33.00	3.08	4.55	—
Hydrogen	14.6	3.512	5.200	2.882
	16.1	3.330	4.929	2.633
	17.9	3.120	4.618	2.318
	18.7	3.030	4.486	2.197
	20.4	2.720	4.029	1.912
Oxygen	70.0	11.9	17.5	18.3
	75.0	11.2	16.5	17.0
	80.0	10.7	15.9	15.7
	85.0	10.1	15.0	14.5
	90.0	9.58	14.2	13.2
Nitrogen	70.0	8.63	12.79	10.53
	75.0	8.03	11.91	9.39
	80.0	7.45	11.04	8.27
	85.0	6.90	10.23	7.20
	90.0	6.36	9.43	6.16
Chlorine	213	30.54	41.40	33.82
	218	30.00	40.65	33.14
	223	29.49	39.92	32.50
	228	28.92	39.19	31.78
	233	28.39	38.47	31.12
	238	27.75	37.60	30.33
	243	27.26	36.93	29.71
	273	23.64	32.00	21.70
	283	22.38	30.30	20.00
	293	21.10	28.60	18.4
	303	19.90	26.90	16.7
	313	18.60	25.20	15.1
Carbon monoxide .	323	17.50	23.70	13.4
	70.0	9.58	12.97	12.11
	75.0	8.96	12.12	10.96
	80.0	8.37	11.34	9.83
	85.0	7.79	10.56	8.74

The Magnitude of $\phi_s(T)/\phi(T)$.

We have already pointed out that the main difference between a molecule in the bulk and in the surface of the liquid arises from the anisotropic oscillations of the molecule in the surface. Regarding the

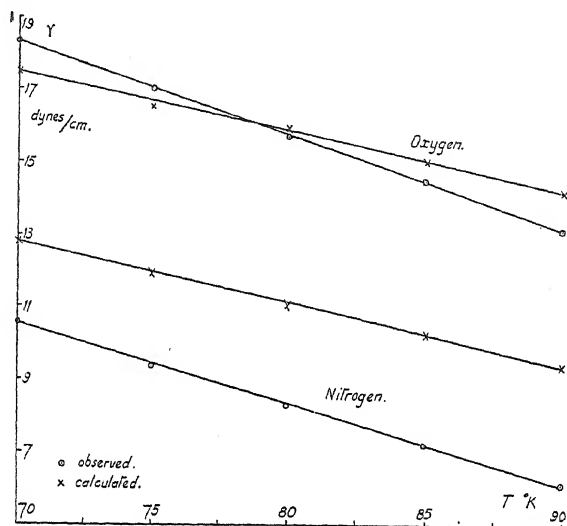


FIG. 4.—Surface tension—temperature curves for oxygen and nitrogen.

TABLE III.

Liquid.	$\partial\gamma/\partial T$ (observed).	$\partial\gamma/\partial T$. (calc.).	
		$A = 4r^2$.	$A = \pi r^2$.
Helium	0.119	0.075	0.1114
Argon	0.260	0.136	0.201
Neon	0.364	0.162	0.239
Hydrogen	0.167	0.118	0.173
Oxygen	0.255	0.111	0.165
Nitrogen	0.224	0.114	0.151
Chlorine	0.154	0.119	0.175
Carbon monoxide	0.304	0.120	0.178

liquid as a quasi-lattice the partition function $\phi(T)$ of a molecule oscillating in three dimensions about a lattice point in the bulk of the liquid can be expressed

$$\phi(T) = \left[1 - \exp \left(-\frac{h\nu}{kT} \right) \right]^{-3} \quad (33)$$

where ν is the characteristic frequency of oscillation in each of the three dimensions. The partition function $\phi_s(T)$ for the oscillations of a molecule about a lattice point in the surface of the liquid can be written

$$\phi_s(T) = \left[1 - \exp \left(-\frac{h\nu}{kT} \right) \right]^{-2} \left[1 - \exp \left(-\frac{h\nu_s}{kT} \right) \right]^{-1} \quad (34)$$

where ν is identical with the characteristic frequency for oscillations in the bulk of the liquid, and ν_s is the frequency of oscillation characteristic of the dimension normal to the surface. The term in which we are interested thus reduces to

$$\frac{\phi_s(T)}{\phi(T)} = \frac{1 - \exp\left(-\frac{h\nu}{kT}\right)}{1 - \exp\left(-\frac{h\nu_s}{kT}\right)} \quad (35)$$

which, if $h\nu$ is small compared with kT , becomes

$$\frac{\phi_s(T)}{\phi(T)} = \frac{\nu}{\nu_s} \quad (36)$$

It is more instructive perhaps to consider the vibration as a linear translational motion along a "free" length, l_t , when the ratio of partition functions becomes

$$\frac{\phi_s(T)}{\phi(T)} = \frac{l_{s,t}}{l_t} \left(\frac{\mu_s}{\mu}\right)^{\frac{1}{2}} \quad (37)$$

where the subscript s refers to the magnitudes in the surface, and μ is the reduced mass of the particular oscillator.*

While there are methods available for evaluating l_t for the bulk of the liquid there seems to us to be no very direct method of evaluating $l_{s,t}$ for the surface. We can, however, calculate what ratios of $l_{s,t}/l_t$ are necessary to give the best correspondence between the calculated and observed values of the free surface energy and surface entropy. These values are given in Table IV.

In computing these values of $l_{s,t}/l_t$, we have chosen a different reduced mass for a molecule in the surface and in the bulk of the liquid. In the bulk of the liquid, the reduced mass for motion in one dimension corresponds to that in the normal mode of vibration of a linear symmetrical three-centre system and is $m/3$, where m is the mass of the molecule. In the surface, however, for motion normal to the surface the reduced mass corresponds more closely to that of a two-centre system and is $m/2$.

Apart from the case of hydrogen the values of $l_{s,t}/l_t$ required to give correspondence between the calculated and observed values of the surface tension are all of the order of $1.2 - 1.3$, and moreover remain fairly constant over the temperature range studied.

The Latent Heats of Vaporisation and the Vapour Pressures.

The latent heat of vaporisation may be calculated from the total energy change accompanying the transference of N molecules from the

* The connection between l_t and ν is given by

$$l_t = \left(\frac{2\pi kT}{\mu(2\pi\nu)^2}\right)^{\frac{1}{2}}.$$

This idea of a free length normal to the surface which differs from the corresponding co-ordinate in the bulk of the liquid arises from the concept of a free volume for the surface molecules which differs from the free volume in the bulk only in respect of the co-ordinate normal to the surface along which the molecular vibration is asymmetric. Equations (33) and (34) represent the effect of this vibrational anisotropy in terms of the fundamental vibrational frequencies in the three dimensions.

TABLE IV.

$T.$	obs.	$= \frac{1}{\sigma} (\chi_s - \chi_0).$	$= \frac{1}{\sigma} \left[\frac{\gamma}{RT} \ln \left(\frac{\mu_s}{\mu} \right)^{\frac{1}{2}} + (\chi_s - \chi_0) \right].$	$\Delta_{1/2}.$	$i_{s,1}/i_1.$
Helium $A = \pi r^2$					
1.4	0.356	0.414	0.380	0.024	1.16
2.3	0.318	0.428	0.374	0.056	1.23
3.1	0.226	0.391	0.318	0.092	1.31
3.9	0.133	0.290	0.206	0.073	1.19
4.2	0.100	0.263	0.176	0.076	1.19
2.21	0.326	0.430	0.377	0.051	1.21
2.28	0.320	0.430	0.376	0.056	1.23
2.47	0.300	0.421	0.363	0.063	1.24
3.21	0.214	0.384	0.309	0.095	1.30
3.81	0.144	0.318	0.234	0.090	1.24
4.13	0.107	0.282	0.195	0.088	1.22
Argon $A = \pi r^2$					
85.0	13.2	17.80	15.88	2.7	1.32
90.0	11.9	16.70	14.66	2.8	1.31
Neon $A = \pi r^2$					
25.08	5.47	6.45	5.61	0.14	1.11
26.06	5.14	6.16	5.30	0.16	1.04
27.06	4.76	5.97	5.09	0.33	1.08
30.04	3.71	5.26	4.31	0.60	1.13
33.00	—	4.55	3.54	—	—
Hydrogen $A = \pi r^2$					
14.6	2.882	3.512	3.233	0.451	1.38
16.1	2.633	3.330	3.026	0.393	1.30
17.9	2.318	3.120	2.788	0.470	1.33
18.7	2.197	3.030	2.685	0.488	1.33
20.4	1.912	3.720	2.354	0.442	1.27
Nitrogen $A = \pi r^2$					
70.0	10.53	12.79	11.36	0.83	1.12
75.0	9.39	11.91	10.37	0.98	1.14
80.0	8.27	11.04	9.43	1.16	1.16
85.0	7.20	10.23	8.54	1.34	1.17
90.0	6.16	9.43	7.70	1.54	1.20
Chlorine $= \pi r^2$					
213	31.2	41.4	38.5	7.3	1.49
218	30.2	40.7	37.7	7.5	1.50
223	29.2	39.9	36.9	7.7	1.50
228	28.3	39.2	36.2	7.9	1.51
233	27.3	38.5	35.4	8.1	1.51
238	26.4	37.6	34.5	8.1	1.50
243	25.4	36.9	34.7	9.3	1.58
273	21.7	32.0	28.5	6.8	1.36
283	20.0	30.3	26.8	6.8	1.35
293	18.4	28.6	25.1	6.7	1.34
303	16.7	26.9	23.3	6.6	1.32
313	15.1	25.2	21.6	6.5	1.32
323	13.4	23.7	19.9	6.2	1.30
Carbon Monoxide $A = \pi r^2$					
70.0	12.11	12.97	11.50	-0.61	0.92
75.0	10.96	12.12	10.58	-0.38	0.95
80.0	9.83	11.34	9.73	-0.10	0.99
85.0	8.74	10.56	8.87	+0.13	1.02

liquid to the vapour phase, which is given in terms of χ_0 and of the free volume available to molecules in the liquid by equation (20). The value of χ_0 can be calculated on the basis of the same model as that we have employed in discussing the surface tension, and will be just twice as great as the value we obtained there; again two values may be calculated, one on the basis of cubical close packing, the other on the basis of hexagonal close packing. Thus

$$\chi_0 = \frac{\rho}{2} \int_a^\infty \frac{\mu}{x^6} 4\pi x^2 dx \quad . \quad . \quad . \quad . \quad . \quad (38)$$

$$= \frac{\pi \rho \mu}{12r^3}$$

$$= \frac{\mu}{20 \cdot 8r^6} \text{ for cubical close packing} \quad . \quad . \quad (39)$$

$$\text{and} \quad = \frac{\mu}{24r^6} \text{ for hexagonal close packing.} \quad . \quad . \quad (40)$$

For the purpose of comparison with experimental results it is simpler to calculate the latent heats at 0°K. , *i.e.*, the value of ΔE at this temperature, for while neither terms $\frac{\partial}{\partial T} \ln \frac{V_g}{eV_1}$ nor $\partial \chi_0 / \partial T$ are linear, the experimental latent heats can easily be extrapolated to absolute zero. Table V gives the radii of the molecules at 0°K. , the calculated latent

TABLE V.—LATENT HEAT OF VAPORISATION.

Gas.	$r_0 \cdot 10^8$.	λ_0 (cubical packing) cal./mole.	λ_0 (hexagonal packing) cal./mole.	λ_0 (experimental) cal./mole.
He . . .	1.505	13.0	20.2	16
A . . .	1.94	1020	1095	1326
Ne . . .	1.58	242	281	312
H ₂ . . .	1.67	167	195	219
O ₂ . . .	1.80	734	854	1920
N ₂ . . .	2.11	853	941	1233
Cl ₂ . . .	2.15	2960	3300	4800
CO . . .	2.10	914	1015	1440

heats for both types of packing and the experimental values. The agreement is very good except in the case of oxygen and of chlorine, the more especially when it is noted that a 2 % decrease in the molecular radius used, results in an increase of about 20 % in the calculated latent heat. With this uncertainty in the term involving the free volumes of the gas and liquid may be neglected.

In the calculation of the vapour pressures from equation (22) the values of χ_0 required are the same as those calculated for the latent heats, and they lead to values of the right order of magnitude. The temperature dependent part of the expression contains two terms, the second of which, however, is uncertain owing to the difficulties in estimating the free volume available in the liquid phase, and it is therefore not possible to calculate accurately the vapour pressure for any given temperature.

Summary.

The free surface energy, the latent heat of vaporisation and the vapour pressure of a liquid, have been calculated from the partition functions of the liquid, surface and vapour phases. The liquid has been assumed to have a given structure, and the potential energy change in moving a molecule from the bulk to the surface calculated for cubically and hexagonally close-packed molecules. The surface free energies and their temperature coefficients so calculated are in good agreement with experimental values for helium, argon, neon, hydrogen, oxygen, nitrogen, chlorine and carbon monoxide. Rotational states may be assumed absent and the difference between the observed and calculated values of the free surface energy attributed to the ratio of the translational partition functions, which may be expressed as the ratio of a free length in the surface to that in the bulk. The values of this ratio calculated for the above gases are of reasonable magnitude. Their latent heats and vapour pressures are also shown to be consistent with the theory.

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THE SURFACE AGEING OF SOLUTIONS.

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It has been pointed out by a number of authors^{1a} that the surface tension of many dilute aqueous solutions, particularly those of paraffin-chain salts, undergoes a very slow decrease, and may take several days, even weeks, to reach equilibrium. On the basis of classical diffusion theory the time should be very much less^{2a} (rarely more than one minute for the concentrations generally employed in such studies). That, indeed, the final surface tension is in many cases attained extremely rapidly has been shown by Bond and Puls.^{2b} With the saturated normal alcohols up to heptylic there was close agreement between theory and experiment, and even with decylic acid at a concentration of 6.4×10^{-5} g. mol./l. the observed values were only some three times those predicted. McBain and Perry³ have also found that for solutions of normal fatty acids up to caprylic the final surface tension is reached in no more than one minute.

With benzopurpurin solutions Doss⁴ has shown that the observed rate of accumulation is some 10^9 times slower than that calculated from the simple collision theory, and the experiments described below with hydrocinnamic acid indicate a factor of the same order (*ca.* 10^7).

Various suggestions have been advanced to account for these anomalously low rates of equilibration. Doss⁴ in particular has suggested that

^{1a} For earlier references see Tartar, Sivertz and Reitmeier, *J.A.C.S.*, 1940, 62, 2375.

^{1b} Nutting, Long and Harkins, *ibid.*, 1496.

^{2a} Langmuir and Schaefer, *ibid.*, 1937, 59, 2400.

^{2b} Bond and Puls, *Phil. Mag.*, 1937, 24, 864.

³ McBain and Perry, *J. Ind. and Eng. Chem.*, 1939, 31, 35.

⁴ Doss, *Curr. Sci.*, 1935, 4, 405; *Proc. Ind. Acad. Sci., A*, 1936, 4, 97; *Curr. Sci.*, 1937, 5, 645; *Kolloid Z.*, 1938, 84, 138; 1939, 86, 205.

the effect can be ascribed to a type of activated adsorption due to an electrostatic potential barrier formed by the adsorbed ions at the interface. Nutting, Long and Harkins^{1b} have recently advanced somewhat similar ideas. McBain and Perry³ suggested that it might be due to the formation of a bi- or poly-molecular leaflet, with the hydrophilic groups not exposed, upon the surface.

As will be shown, however, none of these theories is at all adequate to explain all the experimental facts, and instead it is suggested that a penetration and reorientation factor at the surface, coupled perhaps with some dehydration of the hydrophobic portion, is the predominant factor. In aqueous solutions of ionised substances such as the paraffin-chain salts there is probably a small electrical effect also.

Experimental.

The substances examined, namely, hydrocinnamic acid,³ sodium dodecyl sulphate,^{1b} cetyl sulphonic acid,⁵ and cetyl pyridinium bromide,⁶ have been shown by other authors to give slow adsorption at the concentrations employed in these experiments.

Surface and interfacial tension measurements were carried out by means of a ring and torsion balance applying the corrections of Harkins and Jordan.⁷ At the air/water interface the apparatus allowed the surface tension and the surface potential to be determined simultaneously. The first measurement was usually taken within two minutes of forming the interface. The temperature was 20° C. ($\pm 1^\circ$) in all cases, unless otherwise stated.

Results.

Interfacial Tension Measurements.

During earlier work by the author⁸ it was noticed that at the benzene/water interface no time factor was observed, even with the long-chain sulphates. This observation has been confirmed by further experiments with both benzene and *n*-heptane as the oil phase, and is in agreement with the results of Powney and Addison⁹ on the xylene/water interface. The aqueous solution was 1.93×10^{-3} M sodium dodecyl sulphate, the concentration being well below that at which micellar formation is observed in bulk solution.

When forming the interface, great care has to be taken to avoid disturbances, since these might be expected to increase the rate of adsorption. To overcome this, the interface was initially formed at the base of a conical funnel connected to a vessel containing the aqueous solution, so that it could be slowly increased by a factor of about one hundred with the minimum of disturbance.

The only case in which a time effect was observed was when the aqueous phase was allowed to fall through the oil layer, when the initial I.T. was a few dynes less than the equilibrium value which was attained in some ten minutes. This is doubtless due to an initial interfacial overcrowding by the adsorbed molecules liberated when the unstable emulsion drops coalesce, and supports the earlier observation^{8a} that removal of long-chain ionised compounds from the oil/water interface is not readily brought about.

⁵ Hartley, *J.A.C.S.*, 1936, **58**, 2347, gives critical concentration for micelle formation as ca 5×10^{-4} M.

⁶ Adam and Shute, *Trans. Faraday Soc.*, 1938, **34**, 758.

⁷ Harkins and Jordan, *J.A.C.S.*, 1930, **52**, 1751.

⁸ (a) Alexander and Teorell, *Trans. Faraday Soc.*, 1939, **35**, 727; (b) Alexander and Schulman, *ibid.*, 1940, **36**, 960.

⁹ Powney and Addison, *ibid.*, 1937, **33**, 1243.

Surface Tension and Surface Potential Measurements.

At the air/water interface observations of the surface tension and surface potential confirmed the slow adsorption observed by earlier workers with solutions of sodium dodecyl sulphate (2.0×10^{-3} M), cetyl sulphonic acid (6×10^{-5} M), cetyl pyridinium bromide (0.0112 %), and hydrocinnamic acid (4.00 gms./l.). The direction of change of surface potential indicated that in all cases more molecules were entering the surface film, and all films appeared homogeneous to the movable air electrode.

Hydrocinnamic acid and sodium dodecyl sulphate were then examined in more detail, since these have been thoroughly studied by McBain¹⁰ and Harkins¹¹ respectively.

Hydrocinnamic Acid (see Fig. 1). (Conc. used 4.00 g./l., i.e. 2.67×10^{-2} M). One possible criticism of McBain and his collaborators' work with this acid is the possibility of contamination by very slight traces of heavy metal ions, since these are known to exert a marked influence on fatty

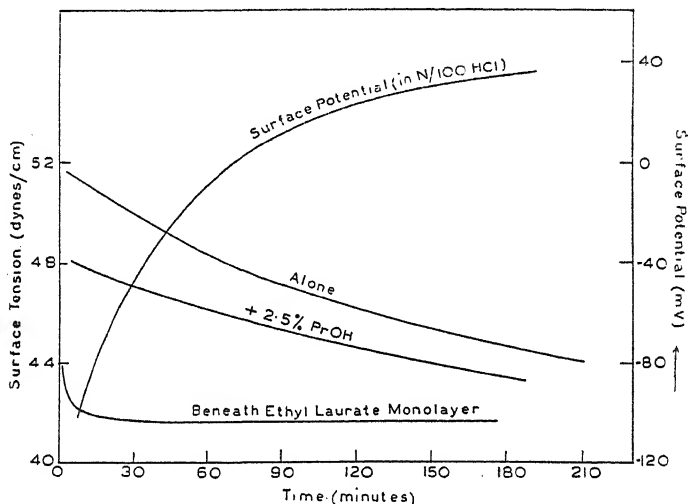


FIG. 1.—Hydrocinnamic acid (4.00 gms./l.) in N/100 HCl.

acid monolayers, even in acid solution.¹¹ Such effects, if due to traces of calcium ions, are negligible at low *pH* values, so the solution was made up in N/100 HCl and a pyrex trough used. Such a solution gave a slow adsorption (see Fig. 1) closely resembling that for the acid alone, except that the results (particularly for the surface potential) appeared to be more reproducible. The surface tension results appear to agree quite closely with those quoted by McBain, Vinograd and Wilson.¹² A simple calculation shows that the observed rate is some 10^7 times less than that calculated on the ordinary diffusion theory.

A solution of the sodium salt of hydrocinnamic acid (also 2.67×10^{-2} M) was then made up by titrating the free acid with NaOH, using phenolphthalein as indicator. This gave no sign whatever of any slow adsorption, the surface tension remaining constant at 72.2 dynes/cm. ($T = 17.3^\circ$) over a period of $2\frac{1}{2}$ hours. As would be expected, this value is much higher than the initial value of the parent acid (ca. 52 dynes/cm.). Freezing-point

¹⁰ Refs. 3, 12, 15b, 29.

¹¹ Harkins and Myers, *Nature*, 1937, **139**, 367; Rideal, Mitchell and Schulman, *ibid.*, p. 625.

¹² McBain, Vinograd and Wilson, *J.A.C.S.*, 1940, **62**, 244.

measurements showed that the salt was not appreciably associated at this concentration, the molar freezing-point constant being 3.71, giving an apparent dissociation of 87.5 %.

Addition of 2.5 % propyl alcohol to the solution of the acid in $N/100$ HCl produced a definite increase in the velocity (see Fig. 1), although the adsorption was still slow. The alcohol alone at the same concentration in $N/100$ HCl gave an immediately attained steady value of 55.2 dynes/cm.

The effect of spreading upon the surface an insoluble monolayer of a piston oil was then examined. Ethyl laurate (spreading pressure (F) 20 dynes/cm.) was chosen, since esters have been shown to have negligible associating tendency with other unionised compounds.¹⁶ As seen from Fig. 1, the time for equilibrium has been enormously reduced, from many hours to about 20 minutes.

Freezing-point measurements showed that at the concentration employed the molecular weight was normal, and accordingly there could

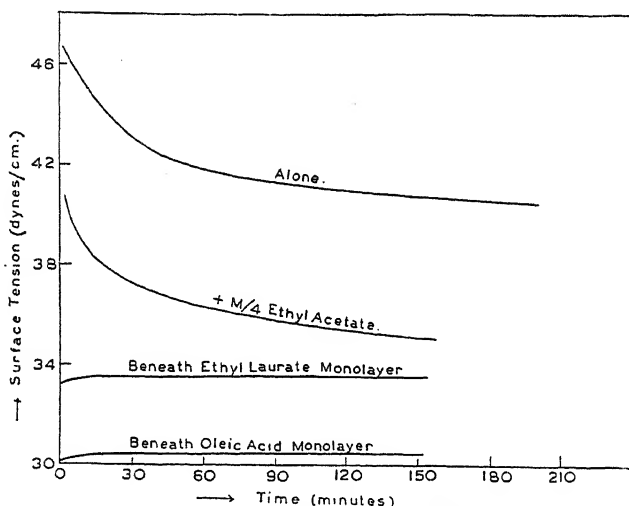


FIG. 2.—Sodium dodecyl sulphate (2×10^{-3} M) in $N/100$ HCl.

be no marked association in solution. The reason for such measurements will be apparent from the discussion.

Sodium Dodecyl Sulphate (see Fig. 2). (Conc. used 2×10^{-3} M). A slow adsorption was obtained both alone and in $N/100$ HCl. In $M/4$ ethyl acetate solution the rate of adsorption was somewhat increased (Fig. 2). ($M/4$ ethyl acetate alone gave a steady surface tension of 51.1 dynes/cm.)

When using monolayers from piston oils of oleic acid (F ca. 33 dynes/cm.) and ethyl laurate ($F = 20$ dynes/cm.) no sign of any slow adsorption could be detected. The lower value obtained with the former is doubtless due to the more powerful association between the sulphate group and the carboxyl as compared with the ester group.^{16b}

Cetyl Pyridinium Bromide (Conc. 0.0112 % in $N/100$ HCl).—Measurements with the ring were rather difficult, particularly at the oil/water interface, on account of the ease with which the ring turned hydrophobic. At the air/water interface the effect of a monolayer of ethyl laurate was to reduce the equilibration time, from several days to not more than a few minutes.

Discussion.

The main points of interest arising from the above experiments can be summarised as follows :—

(a) At the air/water interface very many amphipathic compounds gave a very slow adsorption.

(b) At the oil/water interface the slow adsorption seemed to be invariably completely eliminated.

(c) Monolayers of long-chain compounds (*e.g.* ethyl laurate) removed the time factor, whereas shorter chain compounds (*e.g.* propyl alcohol, ethyl acetate) reduced it but did not eliminate it entirely.

(d) The sign of the surface potential and its variation with time indicated that more molecules were being packed into the adsorbed monolayer, and in no case could any phase change or inhomogeneity be detected.

(e) In the case of hydrocinnamic acid, the time effect was eliminated by formation of the sodium salt.

(f) Addition of N/100 HCl to hydrocinnamic acid had little effect on its adsorption velocity at the air/water interface.

Points from earlier work which have to be considered are :—

(g) The adsorption velocity appears to be of the order expected from classical diffusion if the concentration of the colloidal electrolyte is greater than the critical concentration for micelle formation.¹³

(h) Schulman and Rideal^{16b} and Nutting, Long and Harkins¹⁶ have shown that equilibrium is reached in a few minutes with a long-chain sulphate beneath a long-chain alcohol monolayer.

(i) Slow adsorption can apparently be obtained in non-aqueous solutions (*e.g.* dodecyl sulphonic acid in hydrogenated tetraisobutylene).¹⁴

(j) Adsorption as measured by the microtome and interferometer seems to be completed in a much shorter time than the changes in surface tension.¹⁵

(k) Many substances, *e.g.* caproic, caprylic, indole propionic, and hydrocinnamic acids, give solutions which rapidly form a so-called "surface pellicle" with a definite solution pressure.³

(l) The hydrolysis of an insoluble ester monolayer by OH⁻ ions can be markedly diminished by the presence of ionised soap molecules in the film.^{16a}

Suggested Explanation of Surface Ageing.

The theories advanced by other workers, particularly by Doss, McBain, and Harkins, have been mentioned in the introduction. The evidence presented above shows, however, that all these are untenable.

Firstly, any explanation based upon the repulsion due to electrical forces (Doss and Harkins) must obviously be abandoned in the light of points (b), (c), (e), (f), (h), and (i).

¹³ *E.g.* McBain *et alia*¹², with dodecyl sulphonic acid; Harkins *et alia*¹⁶, with long-chain sulphates.

¹⁴ McBain and Perry, *J.A.C.S.*, 1940, **62**, 989.

¹⁵ (a) McBain and Wood, *Proc. Roy. Soc., A*, 1940, **174**, 286; (b) McBain, Ford and Mills, *J.A.C.S.*, 1940, **62**, 1319.

¹⁶ (a) Alexander and Rideal, *Proc. Roy. Soc., A*, 1937, **163**, 70; (b) Schulman and Hughes, *Biochem. J.*, 1935, **29**, 1236, 1243; Schulman and Rideal, *Proc. Roy. Soc., B*, 1937, **122**, 29; (c) Marsden and Schulman, *Trans. Faraday Soc.*, 1938, **34**, 748.

Considering point (b), earlier work on the equation of state of long-chain ionised compounds at the oil/water interface^{8a} has shown that the areas occupied are, for low interfacial tensions, almost the same as at the air/water interface. Also the changes in the interfacial potential are, at any rate at the benzene/water interface, the same as those found at the air/water interface for the same molecular concentration.¹⁷ Hence no marked difference in the electrostatic potential barrier due to the adsorbed ions would be anticipated, in contrast to the extreme divergence found experimentally. One possible difference between the two interfaces might have been the nature of the adsorbed films, for example, expanded films at the oil/water interface and partially expanded or condensed ones at the air/water. Slow penetration into the condensed films would then explain the difference in accumulation rates. However, this has no support from the above observations on the surface potential, nor from earlier work on ionised compounds at the air/water interface, since films of the C₂₀ and C₂₂ pyridinium bromides and trimethyl ammonium iodides,¹⁸ and palmitic acid on *N*. NaOH substrate,^{16a, 28} have been shown to be of the gaseous type.

The difference in behaviour between the air/water and oil/water interfaces can scarcely be ascribed to the lower interfacial tension at the latter, since even with *n*-heptane (I.T. *ca.* 50 dynes) no time effect is observed, whereas with solutions of about the same surface tension (namely 2.5 % propyl alcohol and *M*/4 ethyl acetate) a diminished, but still definite time-effect, is found.

The efficiency of monolayers of piston oils (*e.g.* ethyl laurate and oleic acid) in eliminating the time effect (points (c) and (h)) appears to be analogous to that of the oil/water interface, since they can be regarded as forming such an interface, even though the thickness is only monomolecular. The use of suitable piston oil monolayers might be made the basis of a more general method for obtaining the final surface tension of solutions of unionised compounds, a point of great value when comparing the observed adsorptions with those calculated from Gibbs' theorem (for example, see ^{15b}). The difference between these insoluble monolayers and the soluble ones from propyl alcohol and ethyl acetate is discussed below.

Point (e) appears irreconcilable with any electrical potential barrier, since complete ionisation of the carboxyl groups would have been anticipated to have decreased the rate of accumulation, instead of making it immeasurably fast. Micelle formation cannot explain the rapid rate, since no appreciable amount can be present (see p. 18).

Also on such a theory the rate should be considerably modified (increased) by addition of electrolytes, owing to a decrease in the depth of the diffuse double-layer, whereas with hydrocinnamic acid addition of *N*/100 HCl produced no marked effect (point (f)). It is true, however, that salts can bring about a marked increase when using colloidal electrolytes,^{1b} but this has been ascribed to their effect on micelle formation, and as pointed out (point (g)) adsorption in the micellar region is almost instantaneous.

Finally, there is the slow adsorption of solutions of lauryl sulphonic acid in hydrogenated tetraisobutylene observed by McBain and Perry,¹⁴ where any marked electrical repulsion would appear to be excluded.

¹⁷ The author, unpublished results.

¹⁸ Adam, *Physics and Chemistry of Surfaces*, 2nd edit., Oxford Univ. Press, p. 129.

Point (l) gives the first definite evidence that an electrostatic potential barrier can be produced at the surface of solutions of ionised substances. Examination of the reaction between ethyl palmitate and N . NaOH at 3 dynes/cm. pressure where the soap is insoluble and remains in the film, shows that the initial rate has been reduced to about one quarter at 50 % reaction. Ignoring the presence of the ester molecules, since these will exert little influence on any electrostatic barrier, the area per soap molecule is about 120 \AA^2 . At 100 % reaction and the same pressure the area would be about 80 \AA^2 , so that the distance apart could only be reduced by a factor of about 11/9. Such a small reduction evidently could not reduce the rate from the factor 4 to one of about 10^7 , the order found in the slow diffusions. Hence, although an electrostatic barrier would seem to be definitely present in such cases, its magnitude is insufficient to account for more than a small part of the discrepancy.

The conclusion thus seems to be inevitable that in no case is the slow accumulation due entirely to any electrostatic repulsive forces arising from the polar head-groups, although they may play a minor part in aqueous media. Equally inevitable appears the conclusion that it is the hydrophobic part of the molecule which in some manner is the rate-determining factor. Hence it is suggested that, provided the compound is molecularly dispersed in solution (true at the concentrations employed in these experiments), the main factor determining the rate of adsorption is the rate of penetration and reorientation in the surface layer, possibly coupled with a dehydration, of the hydrophobic portion of the molecule. The ionised head-group is regarded as playing no direct rôle, except in increasing the solubility for a given chain-length, thus allowing longer-chain compounds to be employed at concentrations unattainable with their unionised analogues.

On general grounds it would be expected that the penetration and reorientation would be assisted by a hydrocarbon environment, particularly if composed of simple molecules such as benzene, xylene, and heptane (point (b)). Piston oil monolayers of ethyl laurate and oleic acid are known to form expanded films in which the hydrocarbon portion closely resembles that of a liquid hydrocarbon,²⁹ so their almost equivalent action is readily explicable (points (c) and (h)). Very short chain compounds, however (*e.g.* propyl alcohol and ethyl acetate), are known to give gaseous films so a diminished effect might be anticipated (point (c)). The reason for the ineffectiveness of the adsorbed monolayer of hydrocinnamic acid in assisting penetration and reorientation of further molecules is probably related to the presence of the phenyl group, since experiments on insoluble monolayers have shown that reorientation on compression is generally rapid for simple straight-chain compounds, but can be very slow when phenyl, branched-chain and other complex groups are introduced.³¹ Such effects should be readily discernible by means of surface viscosity measurements.

Point (e) appears at first sight to be anomalous, since no noticeable time effect was observed under those conditions. However, as has been pointed out (p. 17), hydrocinnamic acid, when existing as the sodium salt, only gives a lowering of about 1 dyne, as compared with some 30 dynes

²⁹ Hartley, *Aqueous Solutions of Paraffin-chain Salts*, Hermann et Cie, Paris, 1936.

³⁰ Sebba and Briscoe, *J.C.S.*, 1940, 106, 114, 128.

(estimated infinity value) given by the unionised acid. At the former value the films are certainly gaseous and the molecules are lying flat on the surface,^{21, 22} so that no packing rearrangement is involved, whereas the lowerings of 25-30 dynes/cm. involve more or less closely packed films, as shown by the following approximate calculation (see also p. 23).

By analogy with short-chain acids (*e.g.* lauric) it can be assumed that adsorbed films of hydrocinnamic acid obey an equation of state of the form $(F - F_0)(A - A_0) = kT$.²³ Taking reasonable values,^{23, 24} such as $F_0 = -10$ dynes/cm., $A_0 = 20$ Å², $kT = 400$, approximate values for

TABLE I.

Surface Tension. (dynes/cm.)	F (dynes/cm.)	A (Å ² /mol.)
52	20	40
47	25	36
42	30	33

A at any given surface tension can be calculated (Table I). If lying flat on the surface the hydrocinnamic acid molecule would occupy some 50 Å², if vertically close-packed about 25 Å².²⁵ Hence for surface tension lowerings of more than 20 dynes, the squeezing-in of further molecules from the aqueous phase will not be easy. For a

molecule to enter the film it must be correctly orientated, and the probability of correct orientation must decrease rapidly as the surface approaches saturation.

On this hypothesis the time factor would be expected to increase with the chain-length and also with the degree of complexity of the hydrophobic portion. As far as the evidence goes, this appears to be approximately true. For example, with the ionised compounds, sodium hexadecyl sulphate is adsorbed some ten times more slowly than the dodecyl compound;¹⁵ although with the more complex compounds such as the long-chain pyridinium and trimethyl ammonium halides it is probably the large head-group which determines the rate. With the unionised compounds lauric acid requires about 30 minutes for equilibrium,²⁶ whereas decylic acid is only adsorbed some three times more slowly than the theoretical rate.²⁰ The latter should be compared with hydrocinnamic acid, where the large phenyl group introduces the marked time factor. Similarly, one can compare phenyl acetic with hydrocinnamic acid, and indole acetic with indole propionic and indole butyric acids,³ where increase of chain-length decreases the rate of adsorption.

Also on the above hypothesis the final surface tension might be expected to be almost independent of the concentration, although the rate of equilibration would, of course, depend on the latter, in agreement with the work of Adam and Shute.⁶

With all the aqueous solutions employed, it has been shown that the solute is molecularly dispersed in all cases, so no explanation of the slow rates could be based upon a slow breakdown on the surface of aggregated molecules present in the solution.

However, in the case of lauryl sulphonic acid in very non-polar solvents (point (i)), where molecular dispersion appears to be most

²¹ Harkins and Fischer, *J. Chem. Physics*, 1933, **1**, 852.

²² Langmuir, *J.A.C.S.*, 1917, 1848.

²³ Langmuir, *J. Chem. Physics*, 1933, **1**, 756.

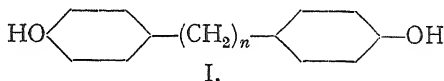
²⁴ Marsden and Rideal, *J.C.S.*, 1938, 1163.

²⁵ Ref. 18, p. 50.

²⁶ Florence, Myers and Harkins, *Nature*, 1936, **138**, 405.

improbable, such a picture may well be true. Further experiments to test this are clearly necessary.

McBain and Perry³ have put forward the view that "surface pellicle" formation, as they term the production of semi-insoluble films on aqueous solutions, may be due to the formation upon the surface of a bi- or poly-molecular leaflet with the hydrophilic groups not exposed. Such formation can, of course, be obtained with soap films and certain liquid crystals, but it has been observed that the formation of insoluble "skins" upon aqueous solutions requires at least two point attachment to the water surface, preferably coupled with a planar ring system, (e.g. I) ($n = 1$ to 6),³² certain porphyrins,³³ and some dihydroxy stilbenes³⁴ (cf. also refs. ²⁷ and ²⁸).



With hydrocinnamic acid examination by the dark-field ultramicroscope of the surfaces of aged solutions showed that micro-crystalline aggregates were formed on compression. This readily explains the difference between fresh and aged surfaces for the spreading of oils²⁹ and also many of the other phenomena observed by McBain and his co-workers.^{3, 12}

The surface potential behaviour would also be very difficult to explain if at some stage bi- or poly-molecular aggregates commenced to form. As shown in Fig. 1, the sign and the direction of change with time are similar to those obtained by compression of monolayers of the insoluble long-chain fatty acids, indicating a slow increase of *similarly orientated* molecules in the surface. An interesting point is the attainment of an almost stationary surface potential while the surface tension is still decreasing. This fits in with the previously suggested picture (p. 22) of a fairly close-packed monomolecular film, in which a small increase of packing would produce a marked fall in surface tension but little effect on the surface potential. Point (j) is also in agreement, since the "surface sandwich" (the composition of which is determined by the microtome) may be in equilibrium with the bulk, and yet by adsorption into the monomolecular surface film of a number of molecules undetectable by a change in total "surface sandwich" adsorption the surface tension can still fall markedly.

It is of interest to recall that the steric hindrance produced by close-packed hydrocarbon chains may be quite large, even for diffusion of simple ionised substances. For example, the short ethyl chain can reduce the diffusion of NaOH by a factor³⁰ of about 8, and the 11 CH₂ groups in brassidic acid when close-packed can slow down that of KMnO₄ by one²⁴ of about 40.

One final point remains for discussion, namely the effect of micelle formation in removing the slow adsorption with solutions of colloidal electrolytes (point (g)). A simple experiment illustrating the mechanism

²⁷ Rideal and Lyons, *Proc. Roy. Soc., A*, 1929, **124**, 333; 1931, **130**, 284.

²⁸ Adam and Miller, *ibid.*, 1933, **142**, 401.

²⁹ McBain and Spencer, *J.A.C.S.*, 1940, **62**, 239.

³⁰ Alexander and Schulman, *Proc. Roy. Soc., A*, 1937, **161**, 115.

³¹ Ref. 18, p. 56.

³² Private communication from Mr. D. C. Pepper.

³³ Stenhagen and Rideal, *Biochem. J.*, 1939, **33**, 1591.

³⁴ Private communication from Dr. J. H. Schulman.

involved is to cover a water surface with a monolayer of a piston oil (*e.g.* triolein-spreading pressure 22 dynes/cm.) and then to eject a small drop of oleic acid (spreading pressure 33 dynes/cm.) beneath the water surface. On rising to the interface, the drop is seen to spread extremely rapidly. Since in the water the interfacial oleic acid molecules would be orientated with their polar groups in the aqueous phase, there is a close analogy with the generally accepted structure of the colloidal electrolyte micelle.¹⁹ A high rate of spreading of micelles in the interface would then be expected.

It was suggested on page 21 that some dehydration of the hydrophobic portion of the molecule might accompany the slow penetration and reorientation to which the slow adsorption has been chiefly ascribed. Evidence that such a factor may be operative comes from several observations of Sebba and Briscoe.²⁰ They observed that monolayers of *n*-docosanol increased their permeability to water from 2 % to 95 % if allowed to stand at large areas (where some of the molecules could lie flat on the water surface) for 20 hours, and that after such long times the film was more soluble and occupied an appreciably greater area. Their explanation, based upon the formation of double molecules on the surface, appears to be rather improbable, and the phenomena can be more simply explained by a slow hydration of the hydrocarbon chains. Unfortunately, this does not give conclusive proof that the actual hydration of the gaseous molecules is a slow process, since the monolayer considered is of the very condensed type and so, even under zero surface pressure, the rate of interchange between the gaseous molecules and those in the condensed islands must be very slow, and may well be the rate determining step. (Examination of the effect of area per molecule on the rate (at large areas), should decide this point). The rate of dehydration and the equilibrium between hydrated and dehydrated chains as functions of the surface pressure, could be obtained by experiments on "hydrated" and "dehydrated" *n*-docosanol films. If also the effect of variation of the chemical nature of the hydrophobic portion (*e.g.* whether straight or branched hydrocarbon chain, saturated or aromatic rings, etc.) could be determined, then it would be possible to decide on the part played by dehydration phenomena in the surface ageing of solutions.

A slow dehydration in the monolayer might quite reasonably be fitted in with all the above experimental evidence, but in view of the uncertainty of such a phenomenon an explanation based upon slow penetration and reorientation appears more satisfactory.

Summary.

Surface tension, interfacial tension and surface potential measurements have been carried out on aqueous solutions of hydrocinnamic acid, sodium dodecyl sulphate, cetyl sulphonic acid and cetyl pyridinium bromide at concentrations where earlier workers have found anomalously slow adsorption at the air/water interface.

This slow adsorption at the air/water interface has been confirmed, and the effect of variation of the conditions, for example, the substrate *pH*, the nature of the interface, addition of capillary active substances to the solution, etc., has been examined. The time factor was found to be eliminated at the oil/water interface and by covering the surface with monolayers of piston oils (*e.g.* oleic acid and ethyl laurate). Addition of capillary active substances (*e.g.* propyl alcohol and ethyl acetate) reduced

the time factor considerably. With hydrocinnamic acid the time factor was also eliminated by formation of the sodium salt.

These new results and earlier work by other authors show that previous theories, based either upon a repulsive electrostatic potential barrier at the interface or upon the formation of poly-molecular layers, are quite inadequate. Instead, it is suggested that the rate determining step is the penetration and reorientation in the surface layer of the hydrophobic portion of the molecule. The question of a slow dehydration in the surface layer is also considered.

Thanks are due to Professor E. K. Rideal, F.R.S., for his continued encouragement, advice, and friendly criticisms.

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EMULSIONS. PART I. MECHANISM OF EMULSIFICATION OF A STANDARD EMULSION IN SODIUM OLEATE SOLUTION AND NATURE OF ADSORPTION AT THE INTERFACE.

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Experiments designed to elucidate the mechanism of emulsification and stabilisation of standard emulsions in a solution of sodium oleate and the nature of the adsorption of soap at the oil-water interface are described in this paper.

The standard emulsion consisted of 60 c.c. of oil dispersed in 40 c.c. of N/30 sodium oleate. Two samples of sodium oleate were used, but no difference in the results obtained with them were noticed. One was a Kahlbaum preparation further purified by recrystallisation from absolute alcohol followed by washing with absolute alcohol and ether. The other was prepared according to the directions of Harkins and Zollmann.¹ The soap solution was prepared with boiled distilled water, and was always used as fresh as possible. It was stored in a bottle from the foot of which it could be drawn off without entry of atmospheric carbon dioxide. The walls of a 500 c.c. conical hard-glass flask, which had been cleaned with chromic acid and steam, were wetted with 40 c.c. of the N/30 sodium oleate. Then 60 c.c. of oil were added and emulsified by Briggs' method² of intermittent shaking as follows. The flask was closed with a cork covered with tin foil and shaken violently by moving the forearm quickly up and down. The downward movement must be powerful, so that the liquid can be heard being smashed against the walls of the vessel. After five of these up-and-down jerks the flask was left for one minute at rest. The treatment was repeated so that in all the mixture had five groups of five shakes, each group being followed by a rest of one minute. The emulsion was then homogenised five times in a hand-driven Pentecrème homogeniser.

¹ W. D. Harkins and H. Zollmann, *J. Amer. Chem. Soc.*, 1926, 48, 69.

² T. R. Briggs, *J. Physical Chem.*, 1920, 24, 120.

Mechanism of Emulsification.

The procedure described led with some oils to the formation of unstable water-in-oil (W/O) instead of oil-in-water (O/W) emulsions. In such cases an O/W emulsion could be obtained by lengthening the period of rest between groups of shakes. Table I shows the types of

TABLE I.

	Benzene.	Decyl Alcohol.	Heptane.
5 shakes			
rest $\frac{1}{2}$ minute .	W/O	W/O	W/O
5 shakes			
rest $\frac{1}{2}$ minute .	W/O	W/O	W/O
5 shakes			
rest 1 minute .	W/O	W/O	W/O
5 shakes			
rest 1 minute .	O/W	O/W	W/O
5 shakes			
rest 2 minutes .	O/W	O/W	W/O
5 shakes			
rest 2 minutes .	O/W	O/W	W/O
5 shakes			
rest 5 minutes .	O/W	O/W	O/W
5 shakes .	O/W	O/W	O/W

emulsion given by three liquids after increasing periods of rest. The type was determined by adding some emulsion either to water or the oil in bulk. In Table II the liquids for which the modified procedure had to be adopted in order to obtain O/W emulsions are given in the column headed B whilst those which gave O/W emulsions with the standard procedure are given

under A. The interfacial tensions of the liquids against water are also listed.

It will be seen that all the liquids with a value of the interfacial tension greater than roughly 42 dynes per cm. belong to group B and those with a lower value to group A. Since our standard emulsion contained 60 per cent. of oil, the quantity of O/W emulsion would be small compared with that of W/O emulsion at the commencement of emulsification. However, since to establish unit area of interface between a liquid of group A and water requires less energy than to do so with a liquid of group B, the droplets of an A liquid are finer and more numerous. Consequently they have a greater chance than

TABLE II.

A.	B.
Aniline . . . 5.8	Carbon tetrachloride 45.0
<i>n</i> -Octyl alcohol . 8.5	Carbon disulphide . 48.4
Ethyl oleate . 21.3	Hexane . . . 51.1
Chloroform . 32.8	Cyclohexane . . 60.6
Benzene . . 35.0	
Toluene . . 36.1	
<i>o</i> -Xylene . . 36.1	
<i>m</i> -Xylene . . 37.9	
<i>p</i> -Xylene . . 37.8	
Higher paraffins . 40.6	

droplets of a B liquid of surviving the rest period and subsequent shaking until they are stabilised by adsorption of sodium oleate, which stabilises only the O/W type. Therefore liquids of group A more readily form O/W emulsions. When the period of rest is increased, there is time for such droplets of a B liquid as have survived to have adsorbed sufficient sodium oleate to be stabilised, whilst on the other hand a larger number of water droplets will have coagulated. The stabilised oil droplets

will survive the second set of shakes, which will again result in the formation of more W/O than O/W emulsion. During subsequent periods of shaking and rest the number of stabilised oil droplets will increase until all the oil has been dispersed in the water. It is well known that adsorption of sodium oleate at liquid-liquid interfaces does not occur instantaneously.

Although O/W emulsions of aniline are very readily formed, they are unstable. Thus the standard procedure with aniline gave the O/W type even during the first group of shakes. However, on pouring the freshly made emulsion into a dry, clean glass vessel large droplets of oil were formed on the walls and on centrifuging a large quantity of oil soon separated. Similarly, Tartar and co-workers³ have found that aniline, although emulsified easily, gave emulsions which were exceptionally readily inverted by sodium chloride. The interfacial tension of aniline against water is the lowest given in Table II. It is therefore easy to understand why aniline so quickly forms an O/W emulsion. The instability of the emulsion must be ascribed to the failure of the sodium oleate to develop a satisfactory interfacial film.

This section may be summarised by saying that in order to understand the process of emulsification it is necessary to distinguish between the reduction of the liquid to droplets and the subsequent stabilisation of these droplets by the emulsifying agent.

Nature of Adsorption at the Oil-Water Interface.

The average diameter of the droplets and the quantities of sodium and oleic acid (including oleate expressed as oleic acid) removed from the aqueous phase by adsorption were determined in standard emulsions of paraffin, benzene and nonyl alcohol (this alcohol was purified in the same way as undecyl alcohol, p. 29).

For the measurement of droplet size a microscope was used with an ocular micrometer standardised with an objective micrometer. A 1/12 oil immersion objective and a no. 5 eyepiece were used. Approximately 0.5 c.c. of standard emulsion was diluted with 100 c.c. of dilute sodium oleate, and a hanging drop slide prepared. Sometimes the method described by Sibree⁴ was used, in which the emulsion is set in gelatine.

For the determination of the quantity of sodium and oleic acid removed from the aqueous phase a large quantity of emulsion was centrifuged in carefully cleaned separating funnels for 20 minutes at 1500 r.p.m. The very stable nonyl alcohol emulsion, however, had to be centrifuged for 7 hours to obtain sufficient equilibrium liquid. The demarcation between cream and equilibrium liquid was always quite distinct. However, the first and last portions of the equilibrium liquid were rejected. To make sure that no coagulation had occurred, the droplet size was redetermined after centrifuging, the cream being diluted with equilibrium liquid. A slight excess of dilute H_2SO_4 was added to 50 c.c. of equilibrium liquid in a separating funnel, and the oleic acid liberated extracted several times with freshly distilled ether. The combined ether extracts were washed with distilled water until the washings no longer gave an acid reaction with lacmoid. After evaporation of the ether the residue was dissolved in neutral alcohol and titrated with N/10 NaOH with phenolphthalein as indicator. The aqueous layers were also collected, and their sodium

³ H. V. Tartar, C. W. Duncan, T. F. Shea and W. K. Ferrier, *J. Physical Chem.*, 1929, **33**, 435.

⁴ J. O. Sibree, *Trans. Faraday Soc.*, 1931, **27**, 161.

content determined gravimetrically as sulphate. As a check, the original sodium oleate solution was analysed at the same time.

From the mean diameter of the droplets and the total volume of oil the number of droplets in 100 c.c. of emulsion was calculated, and from this figure and the mean diameter the total area of the interface was arrived at. Finally, from the total number of molecules adsorbed (sodium oleate and oleic acid) and the interfacial area the average area per molecule was calculated. The results of these experiments and calculations are recorded in Table III.

TABLE III.

Oil.	Average Diameter of Droplets (μ).	Total Area of Interface in 100 c.c. of Emulsion (sq. A.).	Per cent. Na at Interface.	Per cent. Oleic Acid at Interface.	Area per Molecule Adsorbed (sq. A.).
Paraffin, s.g. 0.875	6.0	60×10^{20}	13.3	25.7	29
Benzene	2.3	152×10^{20}	13.6	25.5	74
n-Nonyl alcohol . .	1.0	361×10^{20}	83.7	94.2	47

The figures in the fourth and fifth columns of Table III indicate that in the paraffin and benzene emulsions about 12 % of all the sodium oleate is hydrolysed and that the composition of the adsorbed material is roughly 1 Na-Oleate—1 Oleic Acid, that is acid soap. There does not appear to be much free oleic acid in solution in the oil (compare Nickerson⁵). It is remarkable that much less hydrolysis has occurred in the nonyl alcohol emulsion, in spite of the much larger interface. This may be due to a union between the alcohol and the adsorbed oleate, the alcohol taking the place of the oleic acid in acid-soap. The experiments of Schulman and Hughes⁶ on mixed films of sodium oleate and hexadecyl alcohol at an air-water interface support this view. Schulman and Cockbain⁷ have recently studied emulsions which owe their stability to a molecular complex formed at the interface between an oil-soluble substance and an ionisable water-soluble substance. In our nonyl alcohol emulsion it seems as if the oil-soluble substance is the oil itself. Moreover, it appears that the acid in acid-soap can be regarded as functioning as an oil-soluble substance in the sense of Schulman and Cockbain, for it is well-known that acid-soap is more capillary-active than ordinary soap.

At an air-water interface oleic acid gives a liquid-expanded film, which at no compression occupies about 55 sq. A per molecule and under compression may occupy down to 30 sq. A. In paraffin emulsions to which NaOH had been added to suppress hydrolysis the area per molecule of sodium oleate adsorbed was found by Fischer and Harkins⁸ to vary between 24 and 38 sq. A. Since the lowest figure in the last column of Table III is 29 sq. A, it may be inferred that in no case was the interfacial film more than one molecule thick. In the paraffin emulsion the film appears to have been a liquid-expanded one under compression.

⁵ R. F. Nickerson, *J. Physical Chem.*, 1936, **40**, 277.

⁶ J. H. Schulman and A. H. Hughes, *Biochem. J.*, 1935, **29**, 1243.

⁷ J. H. Schulman and E. G. Cockbain, *Trans. Faraday Soc.*, 1940, **36**, 651.

⁸ E. K. Fischer and W. D. Harkins, *J. Physical Chem.*, 1932, **36**, 98.

⁹ J. H. Schulman and E. G. Cockbain, *Trans. Faraday Soc.*, 1940, **36**, 661.

In the benzene emulsion the interface was not completely covered. Probably benzene, owing to its slightly more hydrophilic character, is better able than paraffin to compete with the soap for a position at the interface. Even if all the soap present had been adsorbed in the nonyl alcohol emulsion, the condition of the film could not have been appreciably altered. If the film is a composite one of soap and alcohol, as already suggested, it is condensed and the stability of this emulsion may be due to this cause.

The Viscosity of Emulsions of some Higher Aliphatic Alcohols.

Standard emulsions of undecyl alcohol exhibited unusual viscosity phenomena.

This alcohol, supplied by Deutsche Hydrierwerke A.G., was further purified by washing with caustic soda and water, drying over sodium sulphate, and distilling under reduced pressure, head and tail fractions being rejected. The m.p. of the purified product was 12° . The viscosity of standard emulsions prepared with it increased on standing to such an extent that the flask could be inverted without flow of the emulsion. On the other hand, standard emulsions of hydrocarbons had viscosities comparable with a thin natural cream. Microscopic examination of the viscous undecyl alcohol emulsion showed that it was very heterodisperse, and contained irregular vacuoles up to $100\ \mu$ across; multiple emulsions were also noticeable. Emulsions of nonyl and decyl alcohols showed a similar increase in viscosity on standing, but did not develop plasticity like those of undecyl alcohol.

The clue to these curious viscosity phenomena lies, we believe, in the fact that at room temperature undecyl alcohol is not much above its melting point. So the composite film of oleate and alcohol may be solid. The oval shape of some of the droplets indicates that their surface is not truly liquid.

Perhaps the multiple emulsions were formed in a way similar to that in which Schulman and Cockbain⁹ consider W/O emulsions are formed, by a solid interfacial film.

Summary.

The mechanism of emulsification of a number of organic liquids in N/30 sodium oleate by a standard method has been discussed, and in particular the influence of the interfacial tension of the oil against water has been described.

It has been shown that the interfacial film is unimolecular. In standard paraffin and benzene emulsions it consists of acid-soap, whilst in nonyl alcohol emulsions there appears to be a composite film of sodium oleate and alcohol. Emulsions of undecyl alcohol exhibit unusual viscosity phenomena.

We are very grateful to Professor H. R. Kruyt for allowing one of us to complete this work in his laboratory.

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EMULSIONS. PART II. PARTIAL COAGULATION OF A STANDARD EMULSION IN SODIUM OLEATE SOLUTION BY SALTS OF SOME BI- AND HIGHervalent METALS.

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Hatschek* noticed that ZnSO_4 was less efficient as a coagulating agent for emulsions in solutions of sodium oleate than CaCl_2 or BaCl_2 when the quantity of electrolyte added was insufficient to react with all the soap present. However, we know of no systematic study of the partial coagulation of emulsions by electrolytes. The coagulation of the standard emulsion in $\text{N}/30$ sodium oleate studied in Part I¹ by varying quantities of salts of bi- and highervalent metals is described in this paper.

Determination of the Volume of Oil Thrown Out.

100 to 150 c.c. of standard emulsion was prepared and left for 10 minutes to allow foam to collapse. Then 7.5 c.c. was run into graduated centrifuge tubes (Fig. 1). Between 0.2 and 1.0 c.c. of $\text{N}/10$ coagulating solution (1 c.c. was equivalent to the sodium oleate in 7.5 c.c. of emulsion) was added to the tubes. Immediately after the addition, each tube was stoppered and turned upside down five times to complete mixing. After half an hour, and again after 48 hours, the tubes were centrifuged for 5 minutes at 2000 r.p.m., and the volumes of oil separated read on their graduated necks. Since the volume of oil thrown out varied from fractions of 1 to 4.5 c.c., centrifuge tubes with different diameters of neck were used. Duplicate determinations were usually made. The presence of jelly at the interface between emulsion and separated oil was sometimes troublesome, particularly when HCl or luteocobaltic chloride were the coagulating agents. Since jellies usually contain only a small proportion of solid, they were included in the volume of oil separated. Such jellies affected the measurements most when a large proportion of the emulsion was broken. Reshaking the tubes after 24 hours did not alter the volume of oil separated when 0.6 c.c. or less of electrolyte had been added, but when 0.8 or 1 c.c. had been added it was usually increased.

The decinormal solutions of the various electrolytes used as coagulating agents were prepared, when possible, from "Analar" materials. The Al in the $\text{Al}_2(\text{SO}_4)_3$ and the Th in the $\text{Th}(\text{NO}_3)_4$ solution were determined

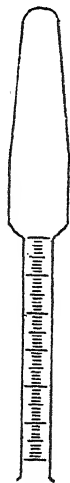


FIG. 1.

* Private communication.

¹ A. R. Martin and R. N. Hermann. This vol., p. 25.

gravimetrically. The Cu contents of the solutions of copper salts were checked electrolytically. The solutions of MgCl_2 and $\text{Mg}(\text{NO}_3)_2$ were prepared by decomposition of the MgO (analar) with acid, and those of CaCl_2 , and on one occasion of BaCl_2 by similar decomposition of the pure carbonate. Hexol salt (hexol-hexaethylenediamine tetracobaltic nitrate, which yields a hexavalent kation) was prepared from cobalt nitrate and ethylenediamine according to the directions of Werner.²

TABLE I.

C.C. OIL N Electro- lyte Added.	Volume of Oil Separated from Standard Xylene Emulsion. (Total Volume of Oil Present, 4.5 c.c.)							
	HCl.	ZnSO_4 .	MgSO_4 .	MgCl_2 .	$\text{Mg}(\text{NO}_3)_2$.	CaCl_2 .	SrCl_2 .	BaCl_2 .
a. 1.0	—	2.91	2.17	3.54	3.87	2.84	2.90	3.48
b. 1.0	4.32	4.42	2.97	4.20	4.19	3.39	3.85	4.35
a. 0.8	—	1.49	1.50	2.25	2.19	1.38	1.84	1.97
b. 0.8	2.91	1.69	1.96	2.77	2.66	1.66	2.03	2.28
a. 0.6	—	0.38	1.01	1.50	1.50	1.01	1.28	1.38
b. 0.6	2.14	0.72	1.20	1.75	1.75	1.22	1.47	1.56
a. 0.4	—	0.24	0.70	0.98	1.05	0.70	0.80	0.83
b. 0.4	1.27	0.37	0.78	1.10	1.15	0.88	0.94	0.98
a. 0.2	—	0.16	0.36	0.53	0.55	0.35	0.43	0.43
b. 0.2	0.66	0.23	0.39	0.54	0.55	0.46	0.49	0.54

	CuSO_4 .	CuCl_2 .	CoCl_2 .	$\text{Al}_2(\text{SO}_4)_3$.	$\text{Th}(\text{NO}_3)_4$.	"Luteo."	"Hexol."
a. 1.0	4.00	4.23	2.91	2.63	4.43	4.45	4.17
b. 1.0	4.30	4.38	4.30	3.47	4.43	4.45	4.32
a. 0.8	2.05	2.63	0.99	2.13	3.24	4.45	2.19
b. 0.8	2.20	3.24	1.55	2.27	3.24	4.45	2.91
a. 0.6	1.40	1.68	0.77	1.61	1.49	1.94	1.69
b. 0.6	1.40	1.74	0.97	1.80	1.70	2.41	2.16
a. 0.4	0.94	1.02	0.49	0.89	0.80	1.38	0.91
b. 0.4	0.94	1.13	0.69	1.09	0.97	1.41	1.25
a. 0.2	0.47	0.56	0.27	0.30	0.44	0.58	0.43
b. 0.2	0.47	0.57	0.35	0.43	0.55	0.71	0.59

a = c.c. of oil coagulated after 30 to 60 minutes.

b = c.c. of oil coagulated after 2 to 3 days.

In Table I are recorded experiments with a standard xylene emulsion (xylene is preferable to benzene for such work because it is less volatile). The xylene was "sulphur free". In Table II are recorded similar experiments carried out at Utrecht, which differed only in that at one time and with the same preparation of emulsion the coagulating powers of the same quantity of different electrolytes were determined instead of those of different quantities of the same electrolyte. In Utrecht more powerful centrifuging was employed (10 mins. at 3000 r.p.m.). Some characteristic results are shown graphically in Fig. 2.

² A. Werner, *Ber.*, 1907, 40, 2113.

TABLE II.

C.c. 0.1 N Electrolyte Added.	Volume of Oil Separated from Standard Xylene Emulsion. (Total Volume of Oil Present, 4.5 c.c.)						
	ZnSO ₄ .	MgCl ₂ .	CaCl ₂ .	SrCl ₂ .	BaCl ₂ .	Al ₂ (SO ₄) ₃ .	Th(NO ₃) ₃ .
a. 1.0	2.97	3.23	3.19	3.32	3.59	3.91	3.49
b. 1.0	3.20	4.05	3.63	3.58	3.63	4.35	3.99
c. 1.0	4.50					4.35	4.45
a. 0.8	1.09	2.24	2.07	2.34	2.72	3.12	2.99
b. 0.8	1.70	2.81	2.21	2.41	3.13	3.20	3.09
c. 0.8	2.45					4.43	3.67
a. 0.6	0.70	1.55	1.30	1.48	1.51	2.09	1.80
b. 0.6	0.79	1.58	1.33	1.52	1.58	2.17	1.80
c. 0.6	1.06					2.20	2.07
a. 0.4	0.35	1.02	0.83	0.86	1.07	1.48	1.09
b. 0.4	0.50	1.02	0.83	0.89	1.07	1.48	1.09
c. 0.4	0.50					1.52	1.09
a. 0.2	0.19	0.53	0.46	0.40	0.49	0.51	0.49
b. 0.2	0.29	0.53	0.46	0.43	0.49	0.53	0.49
c. 0.2	0.29					0.53	0.49

a = c.c. of oil coagulated after about 3 hours.

b = c.c. of oil coagulated after 24 hours, without reshaking.

c = c.c. of oil coagulated after 48 hours, tubes reshaken before centrifuging.

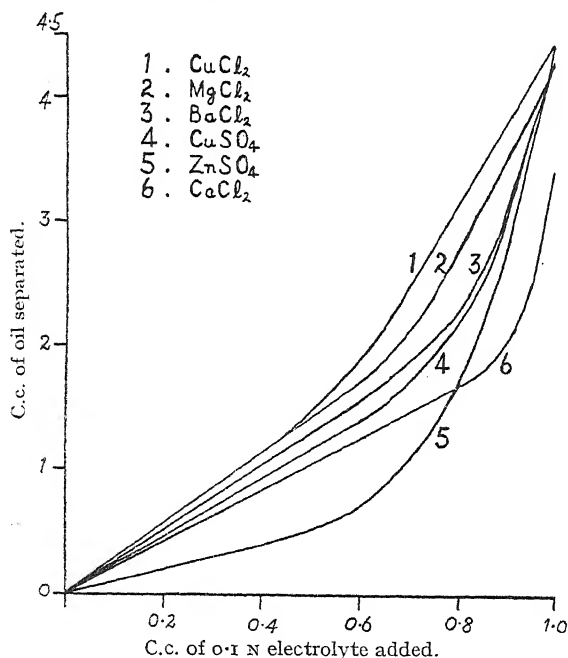


FIG. 2.

Discussion.

If the sodium oleate adsorbed is insufficient for a satisfactory interfacial film, it may be expected that the interfacial area will be diminished by oil separation until such a film can be maintained at the reduced interface (the nature of the interfacial film in standard benzene emulsions has been described in Part I¹; in xylene emulsions it is probably very similar—droplet sizes are the same). Owing to the shape of an adsorption

isotherm, the proportion of the adsorbed film destroyed is, at first, less

than the proportion of all the sodium oleate destroyed by the coagulating salt. But when all the sodium oleate has been destroyed, there cannot be any film left. Consequently, the curve relating volume of oil separated to amount of coagulating salt added is convex to the axis representing the latter quantity—as was always found.

However, this simple theory cannot account for the different coagulating powers of equivalent quantities of various salts observed when these are insufficient completely to break the emulsion. There are few obvious regularities in these specific effects, beyond the order $\text{Ca}^{++} < \text{Sr}^{++} < \text{Ba}^{++}$ for the coagulating powers of the chlorides of the alkaline earths, which is the reverse of the lyotropic series. The effect of valency is slight, and sometimes it is overruled completely, as in hydrochloric acid, which is one of the most powerful coagulants, although both its ions are univalent.

Water-in-oil emulsions formed by soaps of bi- and highervalent metals are too unstable to have influenced the results appreciably, except possibly in the case of magnesium, and, furthermore, the mixture must be shaken after addition of coagulating (inverting) salt to produce them. For instance, when W/O emulsions were prepared by adding to portions of a standard benzene emulsion coagulating salts equivalent to the sodium oleate present, shaking and homogenising, only with magnesium soap was a relatively stable and rather viscous W/O emulsion formed—the bulk of the others broke after a few minutes. Moreover, when mixed soaps obtained by adding quantities of a number of salts equivalent to 50, 60 and 80 % of the sodium oleate in solution were used to emulsify xylene by the standard procedure, magnesium soaps were again exceptional. In the absence of magnesium stable O/W emulsions were formed in the first two cases, and only when 80 % of the sodium oleate had been decomposed was a W/O emulsion obtained—and this broke almost immediately. In each experiment involving magnesium a W/O emulsion was formed, which began to break down after about half an hour. If the tendency of metal soaps to form W/O emulsions had determined the specific effects previously referred to, all salts except those of magnesium would have behaved in much the same way, which was not the fact. One is consequently driven to the idea that the extent to which the interfacial film is destroyed in partial coagulation varies with the nature of the added salt. The reaction between salts of bi- and highervalent metals and sodium oleate was therefore studied.

The Reaction between Salts of Bi- and Highervalent Metals and Sodium Oleate in Emulsions.

(i) **Copper.**—The oil separated by copper salts was a clear blue, independent of its nature. But interaction of equivalent quantities of sodium oleate and copper salts in aqueous solution followed by extraction by an oil gave not a trace of colour to the organic liquid; only after prolonged standing did the copper soap become to some extent oil-soluble. However, addition of oleic acid or sodium oleate, which would give some oleic acid by hydrolysis, made the copper oleate dissolve immediately in the oil. The colour is destroyed by mineral acids, and somewhat less readily by alkali. Although the reaction between sodium oleate and copper salts in aqueous solution gave practically a normal oleate of copper, all the soaps derived from emulsions contained a considerable excess of oleic acid.

A slight excess of $N/10$ $CuSO_4$ was added to a large quantity of standard benzene emulsion. The vessel was immediately turned upside down five times and left for an hour. The separation of the benzene was then completed by centrifuging. On evaporation of the benzene a dark green oil was obtained, which solidified to a soft wax of the same colour. This was dissolved in ether and decomposed by shaking with dilute H_2SO_4 . The oleic acid in the ethereal layer was finally titrated with $N/10$ alkali (for details see Part I, p. 27) and the Cu in the aqueous layer and washings determined electrolytically.

On mixing equivalent quantities of sodium oleate and $CuSO_4$ in aqueous solution, a greenish precipitate was formed, which had to be left for 24 hours before it could be filtered. The light blue-green soap thus obtained was, after pressing, dry to the touch and soluble in benzene. When placed in an oven at 105° , however, large quantities of liquid water separated and left a dark green waxy solid like that obtained on evaporating the benzene separated from an emulsion. This was also analysed.

The results of these analyses are given in Table III (oleate expressed as oleic acid), together with that of the residue from the benzene separated

TABLE III.

Specimen.	Ratio of Molecules of Oleic Acid to Atoms of Copper.
1. From fully broken emulsion .	2.67
2. From fully broken emulsion .	2.73
3. From partly broken emulsion	2.43
4. From reaction in aqueous soln.	1.99

when copper salt equivalent to 80 % of the sodium oleate had been added to the emulsion (thus breaking about one half of it). The first two specimens contained traces of sodium.

If there is oleic acid in the copper soap, there must be the equivalent of metallic hydroxide in the aqueous phase. Therefore, in the second experiment, the solid left in the water and at the interface was analysed. It contained one atom of copper to 0.39 molecules of oleic acid. This basic copper oleate may produce a little unstable W/O emulsion. The separated water was neutral.

The coloured solutions of copper soaps in organic liquids appear to be sols of copper oleate peptised by oleic acid. Soyenkoff³ has studied similar sols of iron and nickel soaps, and Lawrence⁴ has reported complexes of sodium and calcium stearates and fatty acids in "Nujol". The more concentrated solutions obtained by dissolving the waxy copper soaps in an organic liquid were a clear deep emerald instead of blue like the dilute solutions separated from emulsions. The emerald solutions given by the copper soap from an emulsion and by the material prepared in aqueous solution before and after drying in the oven were identical in appearance. Drying over calcium chloride did not change their colour. So although some water may be present it does not play an essential role. Under the microscope (dark field, $\times 700$) only a few small particles in Brownian movement were visible. The reason why the soap prepared in aqueous solution became oil-soluble on keeping is not clear. It may have been partial loss of water (*cf.* Pink's work on magnesium oleate⁵) or liberation of oleic acid. The corresponding sols of copper stearate were very much less stable.

The reactions when a copper salt is added to our emulsion may therefore be pictured as follows. In the water a basic copper oleate is precipitated by reaction with the alkaline sodium oleate (in Part I it

³ B. Soyenkoff, *J. Physical Chem.*, 1930, **34**, 2518.

⁴ A. S. C. Lawrence, *Trans. Faraday Soc.*, 1939, **35**, 702.

has been shown that about 12 per cent. of all the sodium oleate is hydrolysed). Copper oleate is formed at the interface by reaction with the sodium oleate there, and this copper oleate, together with some from the aqueous phase, goes into colloidal solution in the oil, peptised by the oleic acid which was present at the interface. Some basic copper oleate remains in the water.

(ii) **Aluminium.**—On completely breaking a standard benzene emulsion with aluminium sulphate, a colourless solution of aluminium soap in benzene was obtained, which on evaporation yielded a yellowish, transparent, rubber-like substance, which contained 1 atom of aluminium to 4.94 molecules of oleic acid (aluminium weighed as oxide). The separated water was neutral and free from aluminium. The solid suspended in the water and the jelly at the interface together contained 1 atom of aluminium to 0.88 molecules of oleic acid.

(iii) **Zinc.**—The main product was in solution in the separated oil, from which it was recovered as a yellowish-white powdery solid, which contained 1 atom of zinc to 2.05 molecules of oleic acid (zinc weighed as pyrophosphate). The separated water was milky, not alkaline, and contained no zinc in solution. It was centrifuged for an hour—the small amount of solid obtained contained zinc and oleic acid. There was no jelly.

(iv) **Magnesium.**—After an emulsion had been broken by magnesium sulphate, the separated water held an opaque white suspension much thicker than in the case of zinc. This suspension was alkaline, and formed the greater part of the reaction-product. Under the microscope it appeared very heterodisperse with particles up to $2\ \mu$ across. After it had been poured several times through the same filter, a clear filtrate was obtained, which was no longer alkaline. The suspended material was probably magnesium oleate stabilised by magnesium hydroxide. It is this suspension which stabilises the W/O emulsions so readily formed in the presence of "magnesium soap" (p. 33). Pink⁵ has shown that whilst anhydrous magnesium oleate is soluble in benzene, it is precipitated as an hydrated soap on addition of water. Evaporation of the separated benzene gave a yellowish acidic oil consisting of magnesium oleate and oleic acid.

We shall now consider the effect of the reactions described above on the coagulating powers of metallic ions. If a copper salt is added to our emulsion, the interfacial film of acid-soap is destroyed not only by conversion of sodium oleate to copper oleate, but also by removal of oleic acid to peptise the copper oleate in the oil. Consequently, more of the interfacial film is destroyed than if normal copper oleate had been precipitated, and copper salts are powerful coagulants. The fact that when the copper salt added is less than the equivalent of the sodium oleate the excess of oleic acid in the separated oil is smaller (specimen 3, Table III) may be interpreted as due to a competition between the undestroyed sodium oleate and the copper oleate for the oleic acid in the film of acid-soap. The large coagulating power of aluminium sulphate can similarly be traced to the high ratio of oleic acid to aluminium in the oil thrown out. On the other hand, zinc oleate does not remove any oleic acid from the interfacial film. So less of the film is destroyed and zinc sulphate is a poor coagulant. When the coagulating electrolyte is equivalent to all the sodium oleate present, such effects should not alter the volume of oil thrown out, for in all cases there should be no sodium

⁵ R. C. Pink, *J. Chem. Soc.*, 1938, 1252; 1939, 619.

oleate left. The fact that magnesium salts are more powerful coagulants than calcium salts may be due to the formation of some unstable W/O emulsion, which later breaks.

Influence of Dilution of the Emulsion.

The volumes of oil thrown out from a standard emulsion and from two emulsions diluted in different ways, which nevertheless contained the same amount of sodium oleate, were compared. The diluted emulsions were (A) a standard xylene emulsion diluted with an equal volume of water immediately before addition of the coagulating solution (50 c.c. standard emulsion + 50 c.c. water = 100 c.c. emulsion A); and (B) an emulsion prepared in the standard way but with a diluted sodium oleate solution (20 c.c. N/30 sodium oleate + 50 c.c. water + 30 c.c. xylene = 100 c.c. emulsion B). In Table IV are recorded the volumes of oil thrown out from these emulsions by a number of salts, together with the volumes thrown out at the same time from a standard emulsion (column C).

TABLE IV.

C.c. 0.1 N Electrolyte Added.	Volume of Xylene (c.c.) from/after				
	3 hours.	A. 24 hours.	3 hours.	B. 24 hours.	C. 24 hours.
CuSO₄.					
1.0	4.42	4.42	4.36	4.45	4.43
0.8	1.68	2.12	1.68	1.90	2.45
0.6	1.00	1.06	1.00	1.06	1.75
0.4	0.64	0.64	0.68	0.76	1.17
0.2	0.30	0.34	0.34	0.34	0.57
ZnSO₄.					
1.0	—	4.32	—	4.37	4.30
0.8	—	2.05	—	3.74	2.94
0.6	—	0.25	—	0.34	0.76
0.4	—	0.13	—	0.07	0.41
0.2	—	0.09	—	0.05	0.20
CaCl₂.		17 hours.		17 hours.	17 hours.
1.0	—	2.79	—	3.36	2.87
0.8	—	1.10	—	1.77	1.88
0.6	—	0.63	—	0.68	1.44
0.4	—	0.40	—	0.48	0.96
0.2	—	0.20	—	0.17	0.43
Al₂(SO₄)₃.					
1.0	—	4.34	—	4.28	4.35
0.8	—	3.10	—	3.68	3.12
0.6	—	1.62	—	1.84	2.28
0.4	—	0.98	—	1.08	1.48
0.2	—	0.40	—	0.34	0.63

When the quantity of coagulating salt was small, the volume of oil separated was much reduced by dilution. This means that less of the interfacial film had been destroyed, probably because a larger proportion of the reaction had occurred in the bulk of the aqueous phase with precipitation of normal copper oleate. When the coagulating salt was equivalent to the sodium oleate, all the interfacial film was destroyed and the emulsion was

completely broken, whether it was diluted or not. The slight difference between the behaviours of the diluted emulsions A and B may be due to jelly, for there was no such difference when coagulating with copper sulphate, which forms no jelly. Bhatnagar ⁶ noticed that more salt was required to cause inversion when an emulsion was diluted without altering the quantity of sodium oleate present.

Influence of the Nature of the Anion.

The differences in coagulating power between salts with the same kation but different anions, such as MgSO_4 , MgCl_2 , $\text{Mg}(\text{NO}_3)_2$, CuSO_4 , and CuCl_2 (Table I) was confirmed by experiments on the same xylene emulsion with CuSO_4 , CuCl_2 , $\text{Cu}(\text{NO}_3)_2$. The coagulating power of a sulphate is less than that of the corresponding chloride and nitrate, which are equal. This fact can be correlated with the degree of dissociation of these salts. The sulphates of bivalent metals such as Cu and Mg are far from being completely dissociated at the concentrations used, whilst the dissociation of the chlorides and nitrates is practically complete.⁷ A given concentration of the sulphate therefore produces a smaller concentration of bivalent kations than does an equivalent concentration of the chloride or nitrate. It may be supposed that this leads to a larger proportion of the reaction occurring in the aqueous phase in the case of a sulphate and so, as suggested in the previous section, to the coagulation of less oil. For the larger the concentration of an ion the greater will be the extent to which it penetrates the atmosphere of sodium ions around a droplet and reacts at the interface, and this, owing to the removal of oleic acid into the oil by the metal oleate formed, results in the destruction of more of the interfacial film of acid-soap than reaction in the aqueous phase.

Influence of the Nature of the Oil.

Since the character of the interfacial film depends to some extent on the nature of the oil (Part I), addition of the same quantity of coagulating salt to standard emulsions made with different oils may cause the separation of different volumes of oil. For instance, on adding 0.5 c.c. of N/10 copper sulphate to 7.5 c.c. portions of standard emulsions of heptane and decyl alcohol the volume of oil separated in the former case was 1.31 c.c., and in the latter 2.32 c.c. Although the heptane emulsion was much the coarser, it was less sensitive to addition of coagulating salt than the finely divided emulsion of decyl alcohol. However, it has been shown in Part I that in standard emulsions of the higher aliphatic alcohols almost all the soap is at the interface. Such emulsions must be extraordinarily sensitive to coagulating salts, for there is little reserve of soap in solution to maintain the interfacial film.

Summary.

Experiments on the partial coagulation of a standard emulsion of xylene and other oils in sodium oleate solution by salts of bi- and higher-valent metals are reported. The extent to which the interfacial film of

⁶ S. S. Bhatnagar, *J. Chem. Soc.*, 1921, 119, 61.

⁷ C. W. Davies, *The Conductivity of Solutions*, 2nd ed., London, 1933, pp. 110, 138.

acid-soap is destroyed by the formation of sols of metal-soap in the organic liquid peptised by oleic acid is shown to be an important factor in determining the volume of oil thrown out when the quantity of coagulating salt is less than equivalent to the sodium oleate.

We are very grateful to Professor H. R. Kruyt for allowing one of us to complete this work in his laboratory.

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THE INFRA-RED SPECTRUM AND INTERNAL TORSION OF DIMETHYL SULPHIDE.

BY H. W. THOMPSON.

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The infra-red absorption spectra of some volatile alkyl sulphides and mercaptans have recently been measured, with the object of determining the normal vibration frequencies of these molecules and correlating them with other molecular data. The results for ethylene sulphide¹ and methyl mercaptan² have already been published. Present circumstances have delayed publication of the present data on dimethyl sulphide, and in the meantime Fonteyne³ described similar measurements with this substance, some results of which differed in several respects from those which had previously been obtained. The measurements have therefore been repeated, and earlier results confirmed, so that although to a great extent the data now given agree with those of Fonteyne, there are some discrepancies which may affect the correct assignment of normal vibration frequencies. In addition, Fonteyne's calculations appear to err in one respect, and some of his theoretical arguments are thereby invalidated.

Corresponding data on the related molecule dimethyl ether have recently been published by Crawford and Joyce.⁴

Experimental.

The infra-red spectrometer and general procedure have been described previously.⁵ Prisms of sylvine, rock salt, fluorite, and quartz were used, and the resolving power of the instrument is relatively high; the effective slit widths are shown below. The absorption cells were cylindrical glass tubes 21 cm. in length and 3 cm. in diameter, with rock salt end plates fixed on with Apiezon sealing compound. Pressures up to 350 mm. were used. In view of the discrepancies in wave-length of some of the observed bands and those given by Fonteyne, the calibration of the instrument was

¹ H. W. Thompson and D. J. Dupre, *Trans. Faraday Soc.*, 1940, **36**, 805.

² H. W. Thompson and N. P. Skerrett, *ibid.*, 812.

³ *J. Chem. Physics*, 1940, **8**, 60.

⁴ *Ibid.*, 1939, **7**, 307.

⁵ H. W. Thompson, J. W. Linnett, and F. J. Wagstaffe, *Trans. Faraday Soc.*, 1940, **36**, 797.

carefully checked. The wave-length drums were checked against well-established absorption bands of methyl bromide, carbon disulphide, ammonia, carbon dioxide, and ethylene, over all critical regions between 1-15 μ . It is unlikely that any measured wave-length could be in error by more than 0.01 μ , which in most cases is less than the sharpness of the peak. The dimethyl sulphide was a British Drug Houses product. It was first fractionated *in vacuo* but the absorption spectrum appeared to show traces of carbon disulphide. A fresh supply of dimethyl sulphide was tested with triethyl phosphine, but gave no red compound indicative of this impurity. The sample was therefore fractionated *in vacuo*, and then slowly distilled through a long tube packed with solid caustic potash. The middle portion of the distillate was used.

Results.

The curves of Fig. 1 show the absorption over the region 1-16 μ at various pressures, and the positions of the absorption maxima are given in Table I.

TABLE I.

Wave-length (μ).	Wave Number (cm^{-1}).	Intensity.
14.64	683	strong
14.20	704	strong
10.90	917	weak (? doublet)
10.25	976	medium
9.75	1026	very strong
9.62	1040	very strong
8.05	1242	very weak
7.85	1274	very weak
7.67	1304	strong
7.55	1325	strong
7.05	1420	very strong
6.94	1441	very strong
6.87	1460	very strong
6.26	1597	medium
5.82	1718	weak
5.00	2000	medium
4.84	2066	very weak
4.48	2232	medium
4.08 ?	2451 ?	very weak
(3.48)	(2874)	weak
3.42	2924	very strong
3.2	3125	medium
2.72	3676	very weak
2.67	3746	very weak
2.54	3937	weak
2.50 ?	4000 ?	very weak
2.32	4310	medium
2.275	4395	medium
1.71	5848	weak

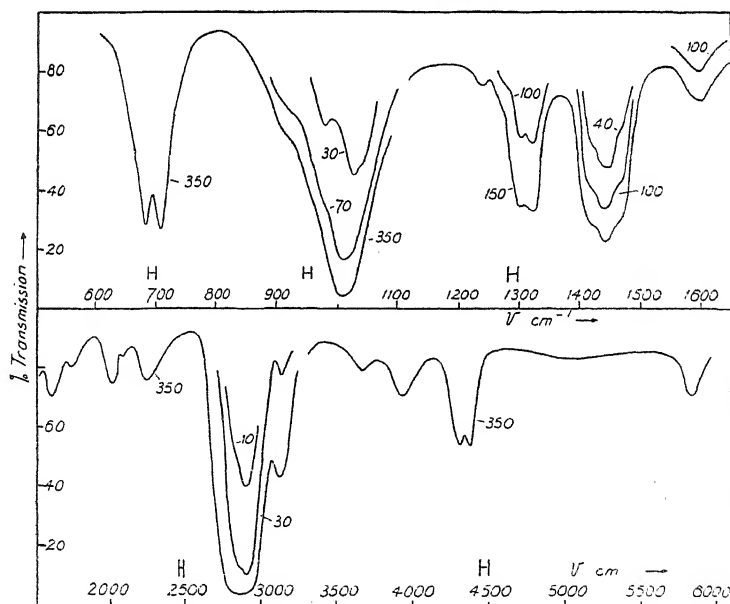


FIG. 1.

(The figures on the curves are the pressures of vapour used in mm. mercury.)

The weak band at 3.48μ appears as a strong shoulder to the main band at 3.42μ ; the doublet band at 7.6μ may also have very weak shoulders at 7.74μ and 7.50μ . The appropriate slit widths are shown in Fig. 1.

Discussion.

The data just given differ from those of Fonteyne in two significant ways. For wave numbers greater than 2000 cm.^{-1} there appears to be a systematic divergence in the values given for the absorption bands. This almost certainly arises in part from the fact that Fonteyne used a fluorite prism in this region, whereas a quartz prism has also now been used giving better resolving power and dispersion. Although the majority of the bands involved are not fundamentals, but combinations or overtones, their exact values are useful corroboration of the values of the fundamentals. The second difference from Fonteyne's data concerns the interpretation of the absorption regions around 7.9μ , 7.6μ , and 6.9μ . The present measurements suggest that the first of these has a double peak, $7.85\text{--}8.05 \mu$ ($1242, 1274 \text{ cm.}^{-1}$); Fonteyne suggests three peaks at $1252, 1262$, and 1274 . The second region at 7.6μ appears now as a doublet, $1304, 1325 \text{ cm.}^{-1}$, whereas Fonteyne suggests another triple peak, $1310, 1323, 1335$. The third region appears in the present work as a triple peak, $1420, 1441, 1460 \text{ cm.}^{-1}$, Fonteyne's values being $1435, 1445, 1459$. These values will be discussed below, but as already explained, the present resolving power is rather greater than that used by Fonteyne, and it is surprising that he was able to resolve some of the very close peaks suggested by his figures, so that his interpretation of them may be questionable.

According to Brockway and Jenkins,⁶ in dimethyl sulphide $r_{\text{CS}} = 1.82 \text{ \AA}$; the other molecular dimensions are less certainly known, but we may take as probable $\text{C—}\hat{\text{S}}\text{—C} = 105^\circ$ and $r_{\text{CH}} = 1.09 \text{ \AA}$. For a C_{2v} symmetry (see below) the moments of inertia are then $43.24, 110.5$, and $148.5 \times 10^{-40} \text{ g. cm.}^2$. The molecule can thus be regarded to a first approximation as a symmetrical rotator having two roughly equal moments of about 130×10^{-40} . The P—R branch separation in a parallel band of this type of molecule (change of electric moment parallel to plane bisecting the C—S—C angle) can be estimated, using the formula of Dennison and Gerhard,⁷

$$\Delta\nu = \frac{S(\beta)}{\pi} \sqrt{\frac{kT}{I_G}},$$

$$\text{in which } \log_{10} S = \frac{0.721}{(\beta + 4)^{1.13}}, \text{ and } \beta = \frac{I_G}{I_A} - 1.$$

In the present case, $\beta = 2.5$ and $S = 1.2$, so that $\Delta\nu = 23 \text{ cm.}^{-1}$. This procedure has been used by Fonteyne, but assuming the same molecular dimensions, he calculates $\Delta\nu = 38.5 \text{ cm.}^{-1}$, which is clearly in error. Fonteyne remarks that this latter spacing far exceeds the doublet spacing observed by him in several bands, although one figure listed by him (26 cm.^{-1}) does not appear to agree with his experimental data. In fact, as will be shown below, the calculated spacing is in fair agreement with at least two band contours, and this consideration affects the assignment of one fundamental. In addition, Fonteyne assigns the Raman

⁶ *J. Am. C. S.*, 1936, 58, 2036.

⁷ *Physic. Rev.*, 1933, 43, 197.

frequency of 742 to the same normal mode as the infra-red value 706. This anomaly is removed by the same correction.

A more exact prediction of the band contours might be sought from the formulae of Badger and Zumwalt,⁸ which apply to asymmetrical

TABLE II.

Class.	Symmetry with Respect to			Total.	Permitted in		Form.	Designation.
	C_2^z	σ_x	σ_y		Raman.	I. Red.		
A_1 (B type band)	s	s	s	7	Yes (p)	Yes (M_z)	CH valency CH valency CH ₃ deformation CH ₃ bending CH ₃ rocking CS valency CSC deformation	ν_1 ν_2 ν_3 ν_4 ν_5 ν_6 ν_7
A_2	s	as	as	4	Yes ($d\bar{p}$)	No	CH valency CH ₃ bending CH ₃ rocking torsional	ν_8 ν_9 ν_{10} ν_{11}
B_1 (C type band)	as	as	as	4	Yes ($d\bar{p}$)	Yes (M_x)	CH valency CH ₃ bending CH ₃ rocking torsional	ν_{12} ν_{13} ν_{14} ν_{15}
B_2 (A type band)	as	s	as	6	Yes ($d\bar{p}$)	Yes (M_y)	CH valency CH valency CH ₃ deformation CH ₃ bending CH ₃ rocking CS valency	ν_{16} ν_{17} ν_{18} ν_{19} ν_{20} ν_{21}

molecules. In their nomenclature $\rho = 1.8$, and $S = -0.7$. It follows, however, that the molecule approaches so closely to being a symmetrical rotator that little is gained by this method as against that given above, particularly when it is remembered that only incomplete resolution can be achieved in the present measurements.

We may, however, expect a $P-R$ branch spacing in each of the A and B type bands which is rather lower than 23 cm.^{-1}

The highest symmetry which the dimethyl sulphide molecule can possess corresponds to the group C_{2v} . There will be 21 fundamentals, which fall into the four classes indicated in Table II. In Fig. 2, C_2^z is the twofold rotation axis zz , and σ_x , σ_y are the symmetry planes perpendicular to xx and yy , σ_x being the plane of the paper and σ_y bisecting the $\text{C}-\hat{\text{S}}-\text{C}$ angle.

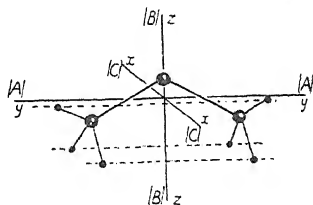


FIG. 2.

⁸ *J. Chem. Physics*, 1938, 6, 711.

A priori, we may expect the CH valency vibration frequencies to have values 2800-3100 cm^{-1} , the deformation frequencies of the methyl groups 1300-1400, and the CS valency vibrations about 700, while the deformation frequency of the CSC chain will be very small, say about 300. The bending and rocking frequencies are less easily predicted, but by analogy with similar molecules the former should lie rather higher than the deformation frequencies, say 1400-1500 cm^{-1} ; the rocking vibrations may, however, have magnitudes over a wide range of, say, 800-1200 cm^{-1} .

The Raman data for liquid dimethyl sulphide have been summarised by Fonteyne. There are differences between the measurements of different workers, but Table III gives the displacements which appear reliable. A very feeble Raman shift of 1609 observed but not interpreted by Fonteyne has been omitted, since it cannot be a fundamental. It might be explained as the combination ($691 + 919$).

TABLE III.

Wave number.	Intensity.	Polarisation.
285	strong	polarised
480 ?	very weak	
691	very strong	polarised
742	strong	depolarised
919	very weak	
1041	very weak	
~1230	very weak	
1325	weak	polarised
1426	medium	depolarised
1440	medium	
2832	weak	polarised
2852	weak	
2911	very strong	polarised
2980	strong	depolarised

The symmetry class A_1 includes all polarised Raman frequencies. We can therefore write at once $\nu_7 = 285$, $\nu_6 = 693$, and $\nu_3 = 1325$, with the two CH valency vibrations ν_1 , ν_2 , probably 2911 and 2832. In the infra-red spectrum the band at 693 cm^{-1} is a doublet type band with the expected spacing, agreeing with this assignment. By analogy with the value of ν_6 , it follows that $\nu_{21} = 742$, a depolarised Raman line. If the first methyl group deformation frequency is 1325, the other may be attributed to the infra-red doublet type band at 1315 cm^{-1} , with spacing 21 cm^{-1} , so that $\nu_{18} = 1315$.

Of the CH valency vibrations, ν_1 and ν_2 have already been assigned. The depolarised Raman line at 2980 does not appear strongly, if at all, in the infra-red, and is attributed to ν_8 . 2852 will probably be one of the three remaining vibrations, and the other two will have values close to this.

The bending and rocking vibrations are not immediately identifiable. The two Raman intervals 1426 (*dp*) and 1440 may be taken to be two bending vibration frequencies; 1426 is assigned to ν_{19} which also appears in the infra-red as a doublet type band 1420-1441, centre 1430. The infra-red band at 1460 may also be attributed to a bending oscillation, and since it does not appear to have doublet contour, to ν_{13} . The fourth bending vibration will certainly be close to 1440.

Of the four rocking vibrations, only three are permitted in the infra-red as fundamentals, if the selection rules are strictly obeyed. As Fonteyne has suggested, however, the Raman intervals of 480 cm^{-1} may

be due to a harmonic of either of the pair of torsional modes, or to a combination of them, so that each of them will have a value of about 240. At room temperatures a vibration of this magnitude will be quite appreciably excited, leading to molecular distortion, and a strict application of the selection rules will be unlikely. If all the data are considered from this standpoint, four magnitudes—917, 1040, 1242, and 1274—seem the most likely values for the four rocking fundamentals.

This assignment leads to a satisfactory interpretation of all the Raman and infra-red data, which is summarised in Table IV.

TABLE IV.

Raman Spectrum.

Wave Number.	Interpretation.	Wave Number.	Interpretation.
285	ν_7	1325	ν_3
480?	$?2\nu_{11}, 2\nu_{15}, (\nu_{11} + \nu_{15})$	1426	ν_{19}
691	ν_6	1440	ν_4, ν_9
742	ν_{21}	2832	ν_2
919	ν_{10}	2852	ν_{12}
1041	ν_5	2911	ν_1
~1230	ν_{14}	2980	ν_8

Infra-red Spectrum.

Wave Number.	Interpretation.	Symmetry Class.
683 } 693	ν_6	A_1
704 }		
917	ν_{10}	A_2
976	$\begin{cases} (\nu_6 + \nu_7) = 978 \\ ?(\nu_{21} + \nu_{11}) = ? \end{cases}$	$\begin{cases} A_1 + A_1 = A_1 \\ B_2 + A_2 = B_1 \end{cases}$
1026	$(\nu_{21} + \nu_7) = 1027$	$B_2 + A_1 = B_2$
1040	ν_5	A_1
1242	ν_{14}	B_1
1274	ν_{20}	B_2
1304 } 1315	ν_{18}	B_2
1325 }		
1420 } 1430	ν_{19}	B_2
1441 }		
1460	ν_{13}	B_1
1597	$(\nu_{18} + \nu_7) = 1600$	$B_2 + A_1 = B_2$
1718	$\begin{cases} (\nu_{19} + \nu_7) = 1711 \\ (\nu_4 + \nu_7) = 1725 \end{cases}$	$\begin{cases} B_2 + A_1 = B_2 \\ A_1 + A_1 = A_1 \end{cases}$
2000	$(\nu_{18} + \nu_6) = 2008$	$B_2 + A_1 = B_2$
2066	$\begin{cases} (\nu_{18} + \nu_{21}) = 2057 \\ 2\nu_5 = 2080 \end{cases}$	$\begin{cases} B_2 + B_2 = A_1 \\ A_1 + A_1 = A_1 \end{cases}$
2232	$(\nu_{18} + \nu_{10}) = 2232$	$B_2 + A_2 = B_1$
2451?	$(\nu_5 + \nu_{19}) = 2466$	$A_1 + B_2 = B_2$
2924	Various CH vibrations	A_1, B_1, B_2
3125	$(\nu_2 + \nu_7) = 3117$	$A_1 + A_1 = A_1$
3676	$(\nu_1 + \nu_{21}) = 3653$	$A_1 + B_2 = B_2$
3748	$(\nu_8 + \nu_{21}) = 3723$	$A_2 + B_2 = B_1$

On the basis of the above assignment, we are in a position to calculate the entropy of the dimethyl sulphide molecule. Twisting about the two C—S bonds will either be restricted, giving the pair of torsional oscillations, or free, leading to internal rotations. The calorimetric entropy has recently been measured by Osborne, Doescher and Yost.⁹ Using the results of Pitzer,¹⁰ and Crawford,¹¹ an estimate can therefore be made of the potential barrier restricting internal torsion. This procedure has been used by Osborne, Doescher and Yost, using as the

⁹ *J. Chem. Physics*, 1940, 8, 506.¹⁰ *Ibid.*, 1937, 5, 469.¹¹ *Ibid.*, 1940, 8, 273.

vibration frequencies a corrected form of the assignment made by Fonteyne. The figures have now been recalculated, using the present more precise frequency assignment and the slightly different moments of inertia.

Thus, we take as frequencies, excluding the two torsional modes :

$$285, 693, 742, 917, 1040, 1242, 1274, 1426, 1440 (2), 1460, 2800, \\ 2832, 2850 (2), 2911, \text{ and } 2980,$$

and for the three principal moments of inertia 43.2, 110.5 and 148.5×10^{-40} g. cm². The moment of inertia of a methyl group rotating about its own axis is taken as 5.2×10^{-40} , and the reduced moment of the two end parts for a free rotation about a C—S bond as 4.9×10^{-40} . In view of minor uncertainties in the values of the molecular magnitudes, it seems unreasonable to give more precise values for these moments, and it will later become clear that small errors in their values do not materially affect the main conclusion about the height of the restricting barrier potential.

Then at 291.06° K. and 365.5 mm., the translational entropy is given by $S_{\text{transl.}} = \frac{3}{2}R \ln M + \frac{5}{2}R \ln T - R \ln P - 2.310 = 39.62$ cal./deg. mole.

The contribution from vibrations other than torsional modes will be

$$S_{\text{vib.}} = R \ln Q + RT \frac{\partial \ln Q}{\partial T},$$

$$\text{in which} \quad \phi = \sum_n e^{-(n+\frac{1}{2})\frac{h\nu_{\text{osc}}}{kT}}$$

giving $S_{\text{vib.}} = 2.34$ cal/deg. mole.

$$\text{For the rigid rotator } Q = \frac{8\pi^2 \cdot (2\pi kT)^{\frac{3}{2}} \sqrt{I_A I_B I_C}}{h^3 \sigma},$$

excluding nuclear spins, and σ being the symmetry number. Then, with $\sigma = 2$,

$$S_{\text{rot.}} = -6.939 + \frac{3}{2}R \ln T - R \ln \sigma + \frac{1}{2}R \ln (I_A I_B I_C) \\ = 21.96 \text{ cal/deg. mole.}$$

Thus the total entropy, excluding that from the torsion, is 63.92. The calorimetric value is 69.35.

For a free rotation about a C—S bond, the entropy contribution is given by

$$S_f = R\{-0.77 + \frac{1}{2} \ln T + \frac{1}{2} \ln I - \ln n\}$$

in which I is the reduced moment of the two rotating ends, and $n = 3$. For restricted rotation, Pitzer has calculated the correction to be applied to this quantity, so that the total contribution now becomes

$$S_t = R\{-0.77 + \frac{1}{2} \ln T + \frac{1}{2} \ln I - \ln n\} - (S_f - S).$$

We now have to determine by trial and error what value of the potential barrier will give such a value to $(S_f - S)$ (read from Pitzer's tables) as to account for the discrepancy of 5.43 cal./deg. mole. For $V = 2000$ cal. $(S_f - S) = 0.88$ and the torsional contribution will be $2 \times 2.64 = 5.28$. The total calculated entropy is therefore 69.20 against the measured value of 69.35. If the slightly more refined procedure of Crawford is followed, the calculated value is about 0.07 units higher, leading to a more exact agree-

ment. The precise value of the restricting potential necessary to give an exact fit must therefore be close to 2000 cal., but in view of the various uncertainties in some of the molecular magnitudes a more precise figure is not justified. The value now given agrees closely with that calculated by Osborne, Doescher and Yost, and is paralleled by the value of 2500 cal. recently estimated by Kistiakowsky and Rice,¹² for the related molecule dimethyl ether. The factors determining the values of the potential barriers are still in doubt. The figures just given, however, suggest another case in which proximity of the end groups may be a controlling factor, the larger dimensions of the central sulphur atom in dimethyl sulphide leading to a greater separation of the two methyl groups and a rather lower potential.

It is hoped shortly to publish similar data on dimethylamine and mercury dimethyl.

I am much indebted to Mr. D. J. Dupré for help in the experimental side of the above work, and also to the Chemical Society and the Royal Society for grants towards the purchase of apparatus.

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¹² *J. Chem. Physics*, 1940, 8, 618.

I. REDOX TITRATIONS OF VAT DYE SYSTEMS.

BY DORIS APPLETON AND A. GEAKE.

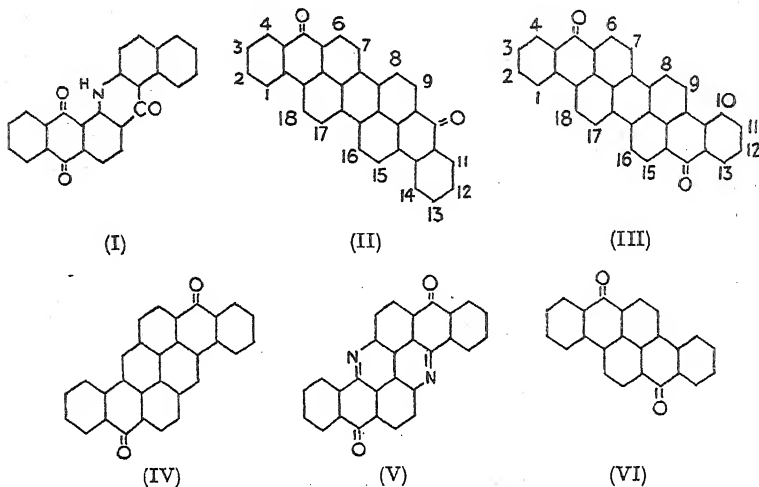
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A previous paper¹ described oxidation titrations of solutions obtained by the reversible reduction in an alkaline medium of anthraquinone and some of its simple derivatives related to the important group of colours known as vat dyes. In accordance with technical nomenclature, such reduced solutions will be called "vats," and the process of dissolution by reduction in an alkaline medium "vatting." The shapes of the redox titration curves showed that semiquinones were formed as intermediate products in the oxidation of those vats examined, and that the extent of semiquinone formation was much greater in the presence of pyridine than in its absence.

The earlier observations included only one derivative in current use as a vat dye, namely, anthraquinone-1 : 2-naphthacridone (formula I), and they have now been extended to a number of vat dyes chosen from among those of published constitutions. Those selected include dibenzanthrone, II, isodibenzanthrone, III, and some of their derivatives, pyranthrone, IV, flavanthrone, V, a few dyes intermediate in molecular size between pyranthrone and anthraquinone, and a few indigoids.

¹ Geake and Lemon, *Shirley Inst. Mem.*, 1937-38, 16, 125-142, or *Trans. Faraday Soc.*, 1938, 34, 1409-1427.

Four dihydroxyanthraquinones have also been titrated. The data for all these substances are collected in Table III (p. 52). The behaviour of dyes with more than one pair of reducible $>\text{CO}$ groups in the molecule will be considered in a separate paper.



Semiquinones.

Most vat dyes are less convenient substances for redox titrations than the simpler anthraquinone derivatives because the very low solubilities of the quinones result in their early precipitation during oxidative titration of the vats. Generally, only that portion of the titration curve which is obtained before the beginning of precipitation is used for the calculation of the normal potentials and the formation constant of the semiquinone, and with vat dyes this portion of the curve is sometimes so short that few or no data can be obtained from it. In almost all cases there was, however, some evidence of semiquinone formation in 50 % pyridine, and in some cases the values of the formation constants (K) could be obtained. The constants that have been determined are lower than those of anthraquinone and its benzoyl derivatives ($\sqrt{K} = 25$ to 290), the highest value of \sqrt{K} for the vat dyes examined in this paper being 20, and the others being in the neighbourhood of 2. In water, precipitation begins earlier than in 50 % pyridine and no evidence of semiquinone formation has been obtainable from the titration curves. The formation constants would be expected to be low, because, as already stated, they are usually lower in water than in 50 % pyridine, and the shapes of the curves do not debar low but real values. In a few cases striking colour changes occur in 50 % pyridine and provide very definite qualitative evidence of semiquinone formation; in most of these cases there is similar, but less pronounced, visual evidence in aqueous solutions. Thus, when conditions are favourable for their detection, semiquinones are found as intermediate products of oxidation even in the absence of pyridine. It is probable that their formation is general, and that the negative evidence of the titrations is a result of small formation constants combined with the very low solubilities of the quinones.

Dibenzanthrone, II, and *isodibenzanthrone*, III, are so insoluble that no exact values of normal potentials could be obtained even in 50 % pyridine, but there is qualitative evidence that semiquinones are formed (see Experimental Section). In these two dyes the quinonoid groups are widely separated from one another, and it seemed legitimate to doubt whether semiquinone formation was possible when they were so far apart. This doubt was resolved by the titration of more soluble derivatives, such as 16 : 17-dihydroxydibenzanthrone, which is sufficiently soluble in 50 % pyridine to permit its vat being titrated without precipitation of the oxidised form. With this substance semiquinone formation was established beyond doubt, the value of \sqrt{K} being 2.6. Semiquinone formation was also definitely established for the dimethyl- and the ethylene-ethers of this substance in 50 % pyridine, the values of \sqrt{K} being nearly the same as for the dihydroxy-derivative itself (1.5 and 2.0, respectively).

The semiquinone formation constants of 3 : 4 : 8 : 9-dibenzpyrene-5 : 10-quinone, VI ($\sqrt{K} = 20$), and pyranthrone, IV ($\sqrt{K} = 2.5$), are intermediate between those of anthraquinone ($\sqrt{K} = 25.2$) and of dibenzanthrone and *isodibenzanthrone*, both of which are assumed to be not greater than unity. The number of carbon atoms in the shortest chain linking the two quinonoid oxygen atoms is ten for dibenzanthrone and *isodibenzanthrone*, and eight, six, and four, respectively, for pyranthrone, dibenzpyrenequinone and anthraquinone; it appears, therefore, that in a series of unsubstituted carbocyclic quinones the value of the formation constant falls as the distance between the quinonoid oxygen atoms increases. This may be due to the same fundamental cause that results in the difference between the two dissociation constants of dicarboxylic acids becoming smaller as the distance between the two carboxyl groups becomes larger. In the latter case the difference between the two constants is ascribed to the opposite influences of carboxyl radicals and of carboxylate ion radicals on the dissociation of a second carboxyl radical, and these influences are smaller when the distance between the two carboxyl groups is greater. The conditions are not quite so simple for the oxidation of the hydroquinone ion because the intermediate product, the semiquinone ion, is not to be regarded as a compound in which one of the negatively charged oxygen atoms has been oxidised and carries an unpaired electron whilst the other remains unchanged, but rather as a symmetrical resonance hybrid in which the two oxygen atoms are in the same state of oxidation. The position may, however, be fundamentally the same, the two negative charges in the dissociated hydroquinone promoting the disappearance of one charge, and the presence of the two carbonyl groups in the quinone promoting reduction. Such effects would facilitate semiquinone formation, and they may be less powerful when the distance between the two active groups is greater.

With anthraquinonoid vat dyes visual evidence of semiquinone formation is seldom very definite, and this is largely because the colours of the leuco-compounds are so intense. With some indigoids conditions are more favourable because the leuco-compounds are almost colourless. For example, with indigo itself there is a striking and abrupt colour change from almost colourless to brown at the point when the oxidation of the excess of sodium hydrosulphite is complete and that of the indigo begins; the colour at the mid-point is a deep red-brown.

Normal and Mid-point Potentials.

The quinone-hydroquinone normal potentials (E_3) at 50° in 50 % pyridine, 0.1 N in sodium hydroxide, range downwards from -133 mv. A more important quantity from the point of view of dyeing and other technical processes, which involve purely aqueous liquors, is the potential of an aqueous vat of standard concentration in reduced dye in the presence of the solid oxidised dye; this is the potential required to reduce the solid form of the dye under standard conditions. It is conveniently

obtained by titrating a vat of double the standard concentration and reading the potential at the mid-point. The concentrations of the vats have been 1 m. mol./l.; at the mid-points the solid forms of all vat dyes are precipitated, and the concentrations of the hydroquinones are then 0.5 m. mol./l. These mid-point potentials are denoted by E_M and their values in 0.1 N aqueous sodium hydroxide at 50° range downwards from about -390 mv.

The quinone-hydroquinone normal potentials depend on the stabilities both of the quinones and of the hydroquinones. These in turn are likely to depend on the number of structures of which each is a resonance hybrid.

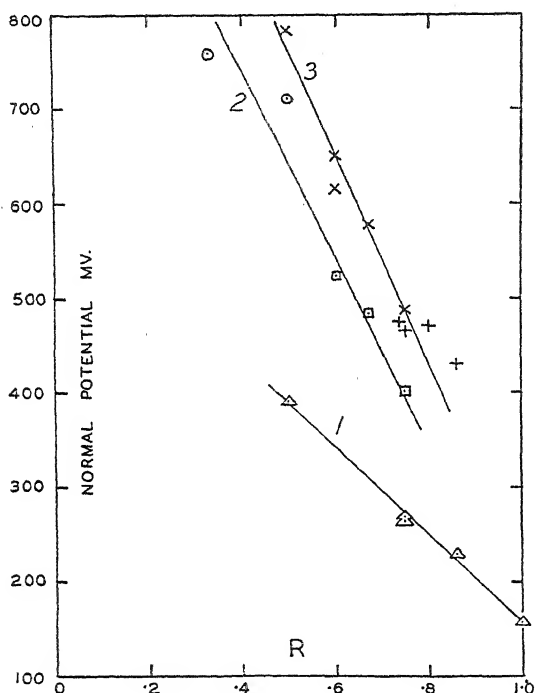


FIG. 1.—Curve 1. Δ *p*-Quinones fused on both sides.
 Curve 2. \square *p*-Quinones fused on one side.
 Curve 3. \circ *p*-Quinones fused on neither side.
 $+$ *o*-Quinones fused on both sides.
 \times *o*-Quinones fused on one side or neither side.

The most important form of resonance of unsubstituted carbocyclic quinones and hydroquinones is probably the Kekulé resonance, and a correlation may, therefore, be expected between the normal potentials of such quinones and the ratios, R , of the numbers of Kekulé structures of the quinones to those of the corresponding hydroquinones. The normal potential would be expected to rise as the value of the ratio falls. Few measurements in alkaline solutions are available for testing such a relation, but the normal potentials of many carbocyclic quinones have been measured in acid solution by Conant, Fieser *et al.*²

² Conant and Fieser, *J. Amer. Chem. Soc.*, 1922, 44, 2480-2493; 1924, 46, 1858-1881; Fieser, *ibid.*, 1928, 50, 465-471; 1929, 51, 3101-3111; 1930, 52,

and the results calculated to a uniform basis of pH 0. When these potentials are plotted against the corresponding values of R (Fig. 1) the general correlation is not good, but the data fall on three lines corresponding with p -quinones in which the quinonoid ring is fused to other rings on both sides, p -quinones in which the quinonoid ring is exposed on one or both sides, and o -quinones. According to Fries³ those fused ring structures are the most stable which contain the largest numbers of benzenoid, as opposed to quinonoid, rings, and it might be considered that it would be better to replace the ratio of the number of structures by the ratio of the total number of benzenoid rings in these structures. Further, since general experience shows p -quinones to be more stable than o -quinones, an alternative, which would allow for this, would be to use the ratio of the numbers of benzenoid plus p -quinonoid rings. The use of these ratios results in some improvement in the general correlation, but the data for the three classes of quinones distinguished above do not fall on one line. When compared at the same values of R , p -quinones with one or both sides of the quinonoid ring exposed have higher normal potentials than p -quinones fused on both sides, and o -quinones have still higher potentials. In these less stable quinones

the quinonoid system $O=C-C=O$ or $O=C-CH=CH-C=O$ is exposed to direct attack, and may be reduced without the rest of the molecule being affected, except in a secondary way. In the anthraquinonoid vat dyes of published constitutions all rings carrying quinonoid oxygen atoms are fused on both sides to other rings, and

TABLE I.

Quinone.	R .	Normal potential, mv.
p -Benzoquinone	0.50	ca. 0
Dibenzanthrone	0.88	ca. - 240
<i>iso</i> Dibenzanthrone	0.90	ca. - 270
3 : 4 : 8 : 9-Dibenzpyrene-5 : 10-quinone	0.92	- 333
Pyranthrone	0.96	- 349
Anthraquinone	1.00	- 512

there are no o -quinones. Table I shows that in measurements made in 50 % pyridine, 0.1 N in sodium hydroxide, and including some anthraquinonoid vat dyes, there is also a correlation of the predicted kind between the values of R and of the normal potential. The approximate normal potential given for p -benzoquinone has been calculated from the value at pH 0 and the two pK values (10.0 and 11.7) of hydroquinone. The normal potentials given for dibenzanthrone and *isodibenzanthrone* are approximate values of the normal potentials of the one-electron oxidations of the hydroquinones to the semiquinones, but the values of the hydroquinone-quinone normal potentials are believed to be not very different from these.

Leuco-pyranthrone and Leuco-flavanthrone.

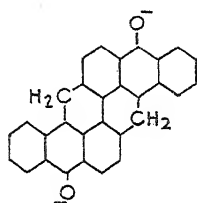
According to Scholl⁴ pyranthrone, IV, yields a cherry-red vat at room temperature but a fuchsin-red vat at a higher temperature; the

5204-5241; Fieser and Dietz, *ibid.*, 1931, 53, 1128-1133; Fieser and Peters, *ibid.*, 1931, 53, 4080-4093.

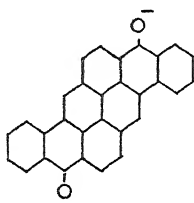
³ Fries, *Liebigs Ann. Chem.*, 1927, 454, 121-324; Fries, Walter and Schilling, *ibid.*, 1935, 516, 248-285. See also Fieser in Gilman's *Organic Chemistry*, Vol. I, pp. 92 *et seq.*

⁴ Scholl, *Ber. deut. chem. Ges.*, 1911, 44, 1448-1452.

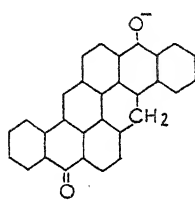
vats used in the titrations at 50° were fuchsin-red. Scholl believed that the two colours were not due to different leuco-compounds, but that the cold vat contained colloiddally dissolved unreduced pyranthrone. Both vats yielded di-acyl derivatives. He gives the formula VII to the leuco-compound, according to which four equivalents of the oxidising agent should be required for its re-oxidation to pyranthrone. The titrations show that only two equivalents are required, and this suggests that the leuco-compound should be formulated as VIII. The alternative formula, IX, does not account for the formation of a di-acyl derivative; also it has the disadvantage as compared with VIII that it exists in only 22 Kekulé forms to the latter's 25. Pyranthrone can be further reduced in methyl alcoholic potassium hydroxide to a brown solution and it is possible that this contains a substance of the formula VII; this might be expected to be less stable than VIII, and thus difficult to obtain, because it exists in only 16 Kekulé forms.



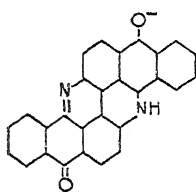
(VII)



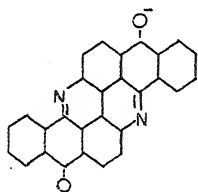
(VIII)



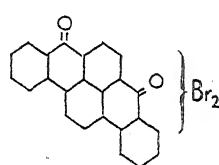
(IX)



(X)



(XI)



(XII)

Flavanthrone, V, differs from pyranthrone only in the replacement of two $-\text{CH}=\text{}$ groups by nitrogen atoms; the ring structure is the same. The ordinary vat is blue, but further reduction leads to a brown vat which is very easily re-oxidised. Scholl and Neovius⁵ found that the blue vat formed only a mono-acyl derivative and that this was not soluble in aqueous or alcoholic potassium hydroxide; they concluded that it contained only one hydroxyl group and gave it the formula X. On the other hand, a disodium salt is formed. In Scholl's view one molecule of sodium hydroxide in this salt takes the place of a molecule of water in the hydrate; many flavanthrone derivatives form hydrates from which the water is driven off only at fairly high temperatures. Formula X agrees with the titrations in requiring that two equivalents of the oxidising agent should be needed for the re-oxidation of the vat. This formula is equivalent to formula IX for leuco-pyranthrone, which was rejected in favour of formula VIII. The reason why pyranthrone reduces to a substance of formula VIII whereas flavanthrone reduces to a substance of formula analogous to IX may be some specific effect of the nitrogen atoms, but a structural reason can be given. For

⁵ Scholl and Neovius, *Ber. deut. chem. Ges.*, 1908, 41, 2304-2328.

pyranthrone, VIII may be expected to be more stable than IX, not only because it exists in more Kekulé forms but also because there are more benzenoid rings in these forms (88 to 82). The behaviour of pyridine, quinoline and their derivatives shows that there is not the same reason for believing that the heterocyclic ring is more stable when it has a benzenoid structure than when it has a quinonoid structure as there is for believing this to be the case for homocyclic rings. If the heterocyclic rings in leuco-flavanthrone are ignored, formula X, although having fewer Kekulé forms than XI (which corresponds with formula VIII for pyranthrone), has more benzenoid rings in these forms, namely, 70 compared with 64.

The quinone-hydroquinone normal potential of flavanthrone in 50 % pyridine, 0.1 N in sodium hydroxide, is 216 mv. higher than that of pyranthrone (see Table III). This difference, which corresponds with the replacement of two $-\text{CH}=\text{}$ groups by nitrogen atoms, is about twice the difference (87 to 112 mv.) calculated from the data of Fieser,* working with acid solutions, for the replacement of one $-\text{CH}=\text{}$ by a nitrogen atom.

Dihydroxyanthraquinones.

The dihydroxyanthraquinones are not vat dyes in a technical sense, but they have been titrated for comparison with anthraquinone. The oxidised forms are soluble in aqueous alkali, and the corresponding vats

TABLE II.

DIHYDROXYANTHRAQUINONES IN WATER.

Positions of OH Groups.	E_1 mv.	E_2 mv.	E_3 mv.	ΔE mv.	\sqrt{K} .
1:2 (20°) . . .	-635	-613	-624	11	1.7
1:4	—	—	-485	—	0.05
1:5	-447	-509	-478	-31	0.33
1:8	-485	-551	-518	-33	0.31
Anthraquinone . .	-480	-428	-454	26	2.6

E_1 = Normal potential of the one-electron oxidation of a hydroquinone to a semiquinone.

E_2 = Normal potential of the one-electron oxidation of a semiquinone to a quinone.

$E_3 = (E_1 + E_2)/2$ = Normal potential of the two-electron oxidation of a hydroquinone to a quinone.

$\Delta E = E_2 - E_3 = E_3 - E_1 = (RT/F) \ln \sqrt{K}$.

can therefore be titrated without precipitation occurring. The semiquinone formation constants in water and 50 % pyridine are given in Tables II and III, respectively, and they are seen to be much lower than those of anthraquinone.

* This value of the difference is obtained from the following normal potentials: 5:8-Quinolinequinone, 557 mv.⁶; 5:8-isoquinolinequinone, 564 mv.⁶; 1:4-naphthaquinone, 470 mv.⁷; differences 87 and 94 mv. α -Naphthaquinoline-quinone, 554 mv.⁸; 9:10-phenanthraquinone, 442 mv.⁸; difference 112 mv.

⁶ Fieser and Martin, *J. Amer. Chem. Soc.*, 1935, 57, 1840-1844.

⁷ LaMer, *ibid.*, 1922, 44, 1954-1964.

⁸ Fieser and Ames, *ibid.*, 1927, 49, 2604-2617.

The normal potentials, E_1 , E_2^\dagger and E_3 of the 1 : 4-derivative are not very different from those of the 1 : 5-derivative either in water or in 50 % pyridine; those of the 1 : 8-compound are lower, and those of the 1 : 2-compound, XVI, are lower still. The constitutional considerations are complicated. Thus, it cannot be assumed that the leuco-compounds, which contain four hydroxyl groups, are fully dissociated, especially in 50 % pyridine, and incomplete dissociation will result in

TABLE III.

(The Values of E_M refer to a Total Dye Concentration of 1 m. mol./l., and thus to a Hydroquinone Concentration of 0.5 m. mol./l.)

Substance.	Formula.	In 50 % Pyridine.						In Water.
		E_1 mv.	E_2 mv.	E_3 mv.	ΔE mv.	\sqrt{K} .	E_M mv.	E_M mv.
Dibenzanthrone	II	ca. -240	—	—	—	—	-328	ca. -640
isoDibenzanthrone	III	ca. -270	—	—	—	—	-407	ca. -700
16 : 17-Dimethoxydibenzanthrone	—	-311	-289	-300	11	1.5	-370	-575
16 : 17-Dihydroxydibenzanthrone	—	-533	-479	-506	27	2.6	—	-573
16 : 17-Dihydroxydibenzanthrone ethylene ether	—	-283	-245	-264	19	2.0	-333	-578
8 : 17-Dimethoxyisodibenzanthrone	—	—	—	—	—	—	-467	ca. -700
Pyranthrone	IV	-375	-323	-349	26	2.5	-449	-660*
Flavanthrone	V	-148	-118	-133	15	1.7	-233	-391
3 : 4 : 8 : 9-Dibenzpyrene-5 : 10-quinone	VI	-417	-249	-333	84	20	-340	-487
Dibromo-4 : 5 : 8 : 9-dibenzpyrene-3 : 10-quinone	XII	ca. -260	—	—	—	—	—	ca. -580
4 : 10-Dibromoanthanthrone	XIII	-340	—	—	—	—	-270	ca. -429
Indigo	XIV	-423	-355	-389	34	3.3	-410	-474
2-Thionaphthen-2'-acenaphthylene indigo	XV	-222	-274	-248	-26	0.39	-257	-408
1 : 2-Dihydroxyanthraquinone (at 20°)	XVI	-707	-647	-677	30	3.3	—	—
1 : 4-Dihydroxyanthraquinone	—	-513	-531	-522	9	0.73	—	—
1 : 5-Dihydroxyanthraquinone	—	-469	-533	-501	-32	0.32	—	—
1 : 8-Dihydroxyanthraquinone	—	-571	-595	-583	-12	0.66	—	—
Anthraquinone	—	-602	-422	-512	90	25.2	—	—

* Sodium sulphate absent.

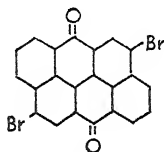
higher normal potentials. Also, each of these tetrahydroxy-compounds can form more than one quinone when oxidised; thus the reduction product of 1 : 2-dihydroxyanthraquinone can form the three quinones 1 : 2-dihydroxy-9 : 10-anthraquinone, 2 : 9-dihydroxy-1 : 10-anthraquinone and 1 : 10-dihydroxy-2 : 9-anthraquinone. When these dihydroxyquinones are dissociated in alkaline solution they differ from one another only in the arrangement of the electrons within the molecule, and the dissolved and dissociated oxidation products may, there-

$\dagger E_1$ and E_2 are defined in Table II.

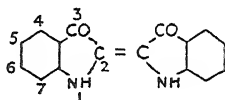
fore, be resonance hybrids of these various structures. In acid solutions the general effect of hydroxyl and alkoxy groups is greatly to depress quinone-hydroquinone normal potentials, the two kinds of groups having approximately equal effects. In alkaline solutions 1:4 and 1:5 substitution have little effect on the quinone-hydroquinone normal potential of anthraquinone either in water or in 50 % pyridine, but 1:8 and 1:2 substitutions depress it considerably. The experimental data may be summarised by the statement that the normal potentials are lower the more closely the four hydroxyl groups in the leuco-compound are grouped together; 1:2-dihydroxyanthraquinone, which has the lowest normal potentials, is the only one of the four compounds which has a β -hydroxyl group.

Experimental.

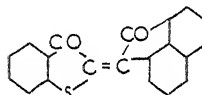
The methods used in making titrations have been described already.¹ Unless otherwise stated all were made at 50°, and the oxidising agent was always either potassium ferricyanide or phenol indo-2:6-dichlorophenol.



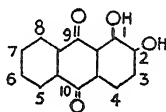
(XIII)



(XIV)



(XV)



(XVI)

The latter has the lower normal potential and is, therefore, milder in its action and less likely to cause unwanted irreversible oxidations; the normal potential is, however, too low for the titration of some dyes. Titrations were always made both in water and in 50 % pyridine at a dye concentration of 1 m. mol./l., and in addition many substances were titrated at lower concentrations in order to postpone the precipitation of the quinone. The data derived from the titrations are collected in Table III.

No values could be obtained for the normal potentials or semiquinone formation constants of vat dyes in water because the quinones are precipitated almost as soon as the oxidation starts. The beginning of precipitation depends not only on the solubility of the quinone, but also on the value of the semiquinone formation constant, since the higher the value of the constant the more semiquinone, and hence the less quinone, is formed during the early stages of the oxidation. Early precipitation is therefore evidence that the formation constant is not high. Since nearly all the constants which it has been possible to measure in water are lower than the corresponding values in 50 % pyridine, and the constants for the vat dyes are not very high in the latter solvent, they cannot be expected to be high in water. Approximate determinations of the solubilities of some of the quinones in water show that these are so small that the early precipitation does not indicate that the constants must be below, say, unity, that is to say, they may be as high as is to be expected from their values in 50 % pyridine.

Generally the only value which could be obtained from titrations in water was that of the mid-point potential, E_M , measured in the presence of the precipitated quinone, and when this was the case titrations in water are not referred to under the individual dyes below. The value of E_M depends on the concentration of the dye, and the data given in Table III refer to a total value of 1 m. mol./l., and hence to a concentration of the leuco-compound of half this value; this is of the same order as those used in dyeing. During the latter parts of the titrations the potentials obtained in the presence of precipitates were often higher than the calculated values, and this appears to be due to the precipitates being incompletely oxidised.¹ This effect is most pronounced when the solubility is least, and is observed chiefly in aqueous solution; in 50 % pyridine it occurs to an appreciable extent only with the most insoluble dyes.

Methods of Calculation.

When precipitation does not begin much before the mid-point of the titration the normal potential E_3 can be read from the curve. Values of \sqrt{K} are calculated from each of the experimental points preceding precipitation by the method already described⁹ and a mean taken; concordant values are usually obtained from all the points except those at the extreme ends of the curve. When precipitation begins earlier and the normal potential E_3 cannot be obtained, a qualitative test for the formation of a semiquinone is to determine whether the first portion of the sigmoid curve is a part of a one-electron or of a two-electron curve. This is accomplished by calculating from the experimental points normal potentials, E_1 and E_3 , for both types of process; the one which correctly describes the oxidation gives concordant values, whilst the other gives drifting values.⁹ If the oxidation is a one-electron process in its early stages, it follows that a semiquinone is formed. The following is another method of which some use has been made. When the value of E_1 has been obtained from the first (sigmoid) branch of the curve as just described, values of the product KL (L is the solubility of the quinone) can be calculated from points on the second branch, obtained in the presence of the precipitated quinone.⁹ If the solubility of the quinone is determined \sqrt{K} can be calculated. This method can lead only to approximate values of \sqrt{K} . In the first place there is always some doubt whether true equilibrium potentials are attained in the presence of the precipitate; the values tend to be too high, and this would result in too high values for \sqrt{K} . Secondly, large errors may occur in determining the solubilities of substances which are so slightly soluble as the anthraquinonoid vat dyes. The method used for determining solubilities in 50 % pyridine is to add a solution of the dye in pyridine to an equal volume of water so that precipitation occurs and, after prolonged standing at 50°, to filter through the finest grade of fritted glass filter. The colour of the filtrate is intensified by reduction to the leuco-compound, and is compared with those of vats of known concentrations. Generally a good match is not obtained between the two vats, and the measured solubilities are likely to be maximum values; high values lead to low values of \sqrt{K} . In some cases both \sqrt{K} and KL can be obtained from the titration curve, and the value of the solubility calculated from these can be compared with the measured value.

Dibenzanthrone (Formula II).—An already purified sample was recrystallised three times from nitrobenzene. When titrated in 50 % pyridine precipitation began very early, but when the concentration was diminished to 0.05 m. mol./l. precipitation was delayed until the oxidation was about 20 % complete. Calculation from the short first branches of

⁹ Geake, *Shirley Inst. Mem.*, 1937-38, 16, 111-124; or *Trans. Faraday Soc.*, 1938, 34, 1395-1409.

the curves gave constant values for the normal potential of a one-electron process, and thus provided qualitative evidence that a semiquinone was formed. When titrated in water, particularly large rises of potential were obtained during the latter part of the titration, and the end-point was completely obscured; no reliable value of E_M could be obtained. Similar, but smaller, rises were obtained in 50 % pyridine, and this had the effect that false end-points were obtained when the oxidising agent was phenol indo-2 : 6-dichlorophenol, which does not raise the potential above about -150 mv. Potassium ferricyanide can raise the potential to 300 mv. and the true end-point was obtained when this was used.

isoDibenzanthrone (III).—A purified commercial product was recrystallised three times from 700 parts of nitrobenzene. When titrated in water there was no break corresponding with the completion of the oxidation of the excess of sodium hydrosulphite used in vatting; this was apparently due to the oxidation of the dye beginning at a very low potential. Titrations were, therefore, made in 5 % pyridine. A break was then obtained and the precipitation of the dye began almost immediately at a potential of about -660 mv. In spite of the low potential which must be required for the reduction of the solid quinone, this dye is not in practice difficult to vat. Even in 50 % pyridine and at a concentration of 0.1 m. mol./l. precipitation began before the oxidation was 10 % complete, and the most that could be obtained was qualitative evidence, similar to that described for dibenzanthrone, in favour of semiquinone formation.

16 : 17-Dimethoxydibenzanthrone.—The well-known vat dye Caledon Jade Green is stated to have this constitution.¹⁰ The commercial material was recrystallised several times from 1000 parts of pyridine or 200 parts of nitrobenzene, and the purity of the product was confirmed by spectral methods. Many titrations have been made in 50 % pyridine at dye concentrations of 1 to 0.02 m. mol./l. At the higher concentrations, precipitation began early, and only qualitative evidence of semiquinone formation could be obtained. At concentrations not greater than 0.1 m. mol./l. precipitation was postponed long enough for the first branches of the curves to be fully analysed, and in all cases values of \sqrt{K} near to 1.5 were obtained. Although this value of \sqrt{K} requires that nearly half the dye must be in the form of the semiquinone at the mid-point of the titration (in the absence of precipitation) no visual evidence of semiquinone formation was observed.

16 : 17-Dihydroxydibenzanthrone ethylene ether.—This is the constitution given to Caledon Dark Blue G,¹¹ and it differs from Caledon Jade Green X only in the replacement of two methyl groups by one ethylene group. The material used was a purified commercial sample. When titrated at the usual concentration of 1 m. mol./l., precipitation began early even in 50 % pyridine. At one-tenth of this concentration precipitation was postponed until about the mid-point, and the first branches of the curves could be fully analysed. The value obtained for \sqrt{K} , namely 2.0, differed only slightly from that found for Jade Green, and these two values for closely similar substances may, therefore, be considered to confirm one another. There was no visual evidence of semiquinone formation. The vat was a deep blue; during the early stages of the oxidation the colour became duller and greyer and the precipitated oxidant was a dull blue.

16 : 17-Dihydroxydibenzanthrone.—The material used was a specially purified commercial sample. The presence of the two hydroxyl groups did not postpone appreciably the beginning of precipitation in water as compared with Jade Green, but in 50 % pyridine no precipitation occurred. A complete sigmoid curve was thus available for analysis.

¹⁰ *Colour Index* No. 1101, Thomson, *J. Soc. Dyers and Col.*, 1936, 52, 247-252.

¹¹ Rowe, *The Development of the Chemistry of Commercial Synthetic Dyes* (1856-1938), Institute of Chemistry Monograph, 1938.

The values of \sqrt{K} calculated from different points on the curve showed a definite drift, being smallest for points near the centre and becoming larger as the points used became nearer to either end of the curve. Titrations in 50 % pyridine were made also with vats from 16:17-diketo-dibenzanthrone. This substance was prepared from the purified dihydroxy-compound by oxidation with chromic acid in dilute sulphuric acid. Reduction by four equivalents should lead to the same vat as that given by the dihydroxy-compound, and the titration curve was in fact similar, drifting values of \sqrt{K} being obtained. Duplicate titrations did not agree as well as usual; in one titration the values of \sqrt{K} were constant over a considerable stretch of the curve, and it is this constant value ($\sqrt{K} = 2.6$) which is recorded in Table III. It was not found possible to obtain a curve corresponding with the oxidation of the dihydroxy-compound to the diketo-compound, even when potassium ferricyanide was the oxidising agent. Visual evidence of semiquinone formation was indefinite. The vat was a deep blue; when oxidised this became duller and greener, then a very deep bright green, and finally a less intense bright green.

Drifts in the value of \sqrt{K} , such as described above, can be observed only when calculations are made from point to point along the titration curve, and this has not usually been done in the titrations recorded in the literature; the effect may, therefore, be not uncommon. Titrations of vat dyes are not very favourable for its observation on account of the interruptions caused by the precipitation of the quinones, and few suitable titrations have been published in sufficient detail for recalculation. A drift in the value of \sqrt{K} is found in a titration of pyocyanin by Elema¹² in which the value rises from a minimum of 5.5 for points near the centre of the curve to about 6.4 for points near fractional oxidations of 0.1 and 0.9. In cases of this kind, Elema's method for the calculation of \sqrt{K} from the slope of the curve at the mid-point¹³ gives the same result as is given by the method used in this work for points near the centre of the curve, and Michaelis' method, using the index potential,¹⁴ gives the same result as is obtained from points near to fractional oxidations of 0.25 and 0.75.

8:17-Dimethoxyisodibenzanthrone.—Caledon Ming Blue X is stated¹¹ to have this constitution and a purified commercial sample of this dye was used. When titrated in water it behaved like the parent substance, isodibenzanthrone, in oxidising at so low a potential that there was no break corresponding with the completion of the oxidation of the excess of sodium hydrosulphite. In 5 % pyridine a good curve was obtained, but both in this and in 50 % pyridine precipitation began so early that no evidence regarding semiquinone formation was obtained. Even at a concentration of 0.05 m. mol./l. in 50 % pyridine precipitation began when the oxidation was about 15 % complete. The first branches of a number of curves did not give consistently more constant values for the normal potential of a one-electron process than for that of a two-electron process, so that for this dye there is no evidence for the formation of a semiquinone.

Pyranthrone (IV).—The commercial material was recrystallised four times from 1000 parts of nitrobenzene and the purity of the product was confirmed by spectral methods. When titrated in water the dye was oxidised at so low a potential that the first break was not sharp; a better curve was obtained in 5 % pyridine. When titrated in 50 % pyridine at a concentration of 0.015 m. mol./l. the magenta coloured vat became blue

¹² Elema, *Rec. trav. chim.*, 1931, **50**, 807-826; Table No. 3.

¹³ Elema, *J. Biol. Chem.*, 1933, **100**, 149-153; *Rec. trav. chim.*, 1935, **54**, 76-78.

¹⁴ Michaelis, *J. Biol. Chem.*, 1932, **96**, 703-715; *Chemical Reviews*, 1935, **16**, 243-286.

during the early stages of the oxidation; precipitation of the orange quinone began near the mid-point, and full analysis of the curve was possible, giving a value of 2.5 for \sqrt{K} . This is one of the few cases in which there was clear visual evidence of the formation of an intermediate compound. The titrations showed that two equivalents of sodium hydro-sulphite were required to vat the dye, and two equivalents of the oxidising agent for the re-oxidation of the vat to the original quinone. The solubility of the quinone can be calculated from the value of \sqrt{K} obtained from the first branch of the curve and that of KL obtained from the second branch, and two titrations gave the values 5 and 2.6×10^{-4} m. mol./l., respectively. The measured solubility is 5×10^{-4} m. mol./l., but as pointed out on page 54 this is likely to be a maximum value.

Flavanthrone (V).—This is stated by Scholl¹⁵ to be crystallisable from quinoline, but, although the solvent was freshly distilled, the crystals obtained from it were browner than the original yellow crude flavanthrone. Since flavanthrone is very easily reduced, and the vat is blue, it appeared likely that the browning was due to reduction. Purification was, therefore, limited to extraction with dilute hydrochloric acid until the dye was free from antimony derived from the antimony pentachloride used in its manufacture. All the titrations were made with the ordinary blue vat, and they show that this requires two equivalents of an oxidising agent for re-oxidation to flavanthrone. When this vat was titrated at a concentration of 1 m. mol./l. in 50 % pyridine precipitation began early, and the best results were obtained from titrations at concentrations of 0.1 and 0.03 m. mol./l.; at these concentrations precipitation was postponed until the oxidation was about 18 % and 30 % complete, respectively. The first branches of the curves yielded concordant values for the normal potentials of a one-electron process, but drifting values for that of a two-electron process, and thus provided qualitative evidence of semiquinone formation. The value of \sqrt{K} can be obtained from that of KL obtained from the second branches of the curves and a measured value of the solubility, namely 7×10^{-7} m. mol./l. Three experiments agreed in giving values of \sqrt{K} between 1 and 2. There was no visual evidence of semiquinone formation.

3 : 4 : 8 : 9-Dibenzpyrene-5 : 10-quinone (VI).—This substance was chosen for titration because its molecule is intermediate in size between those of anthraquinone and pyranthrone. Indanthrene Golden Yellow GK¹¹ was recrystallised three times from 200 parts of nitrobenzene. In 50 % pyridine at a concentration of 1 m. mol./l. precipitation began shortly after the mid-point; full analysis of the curve was, therefore, possible, and the results were confirmed by titration at a lower concentration at which no precipitation occurred. There was also striking visual evidence of semiquinone formation; the vat was a bright clear red, the colour at the mid-point was blue, and the precipitated quinone was golden yellow.

Dibromo-4 : 5 : 8 : 9-dibenzpyrene-3 : 10-quinone (XII).—The material used was commercial Indanthrene Scarlet 4G,¹¹ recrystallised three times from 400 parts of nitrobenzene. In 50 % pyridine at a concentration of 0.5 m. mol./l. precipitation began when the oxidation was 20-25 % complete. The first branches of the curves gave constant values for the normal potential of a one-electron process, but drifting values for that of a two-electron process, thus giving qualitative evidence of semiquinone formation. There was no definite visual evidence; the vat was red and the precipitated quinone orange, whilst at the mid-point the colour was a dull brownish grey.

4 : 10-Dibromoanthranthrone (XIII).—The material used was commercial Indanthrene Brilliant Orange RK,¹¹ recrystallised three times from 450 parts of nitrobenzene. In 50 % pyridine precipitation began

¹⁵ Scholl, *Ber. deut. chem. Ges.*, 1907, 40, 1691-1702.

shortly before the mid-point, and the steepness of the part of the curve immediately preceding precipitation showed that but for this there would have been a large central break corresponding with a high value of \sqrt{K} . The slope of the sigmoid part of the curve was, however, slightly greater than that calculated for a one-electron process, and this is most likely due to the sample being a mixture of isomeric dibromo compounds or of compounds at different stages of bromination. The slope of the curve was slightly greater after recrystallising than before, and it was evident that further recrystallisation from nitrobenzene would not separate the components effectively. Nevertheless, it seems reasonable to conclude that these substances form semiquinones, and this is supported by the colour changes; the deep violet vat becomes paler and bluer before the mid-point, although the precipitated quinone is orange.

Indigo (XIV).—A specially purified sample was used. Indigo is more soluble than the majority of anthraquinonoid vat dyes, and when titrated in 50 % pyridine at a concentration of 1 m. mol./l. precipitation did not begin until the titration was 80 % complete. Thus a sigmoid curve capable of full analysis was obtained, and the points yielded concordant values for \sqrt{K} . There was also definite visual evidence for the formation of an intermediate compound, as already described on page 47. In water at a concentration of 0.15 m. mol./l. precipitation began when the titration was about 20 % complete and calculation from the first branch of the curve yielded concordant values for the normal potential of a two-electron process but drifting values for that of a one-electron process; this indicates that if an intermediate product is formed in water its formation constant must be quite low. Nevertheless, at the first potential break there was an abrupt colour change similar to that in 50 % pyridine; this is good evidence that an intermediate product is in fact formed, although the formation constant is too low for its formation to be detected by the shape of the titration curve.

Many attempts have been made to titrate recrystallised Durindone Blue 4BC, which is stated to be 5 : 7 : 5' : 7'-tetrabromoidigo,¹⁶ but concordant results could not be obtained either in water or in 50 % pyridine. The colour changes were, however, similar to those of indigo.

The titrations of indigo and other indigoid dyes were made in 0.01 N sodium hydroxide because approximately this concentration is used in technical dyeing.

2-Thionaphthen-2'-acenaphthylene indigo (XV).—This is the constitution given to the dye Durindone Scarlet Y,¹⁷ and a recrystallised sample of this was used for the titrations. The vat is a deep reddish-blue, so that, unlike indigo, it possesses no special advantages for the visual observation of the formation of an intermediate product; no such visual evidence was in fact observed. The first branches of the curves obtained from titrations in water also gave no definite qualitative evidence of the formation of an intermediate compound. For titrations in 50 % pyridine phenol indo-2 : 6-dichlorophenol gave hardly high enough potentials to yield sharp end breaks, and potassium ferricyanide caused some irreversible oxidation at the end-point. The slight uncertainty about the end-points could, however, have only small effects on the values of the normal potentials and of \sqrt{K} . The value found for \sqrt{K} is small but duplicate titrations gave concordant values throughout.

1 : 2-Dihydroxyanthraquinone (Alizarin) (XVI).—A sample of laboratory reagent quality was resublimed three times. On account of the solubility of alizarin in aqueous sodium hydroxide, it can be titrated both by reduction with sodium hydrosulphite and then by re-oxidation with phenol indo-2 : 6-dichlorophenol. Visual evidence, as well as the analysis of the titration curves, indicates that a semiquinone is formed.

¹⁶ *Colour Index*, No. 1184.

¹⁷ *Ibid.*, No. 1228.

Thus the reduced solution is a pale orange-red and the fully oxidised solution is deep violet in water, but the additions of the first portions of the oxidising agent turned the solution yellower instead of bluer and the colour became a deep yellow-brown before becoming green and then violet. In 50 % pyridine the colour changes are similar except that the fully oxidised solution is blue rather than violet. The titrations were made at 20°.

1 : 4-Dihydroxyanthraquinone (Quinizarin).—The titrations were made with a sample prepared from purified intermediates and recrystallised. The slope of the curve obtained from titration in water was within the experimental error of that calculated for a two-electron process, so that not more than a small proportion of a semiquinone can have been formed. In 50 % pyridine the curve was steeper and yielded concordant values for \sqrt{K} , and there was also visual evidence of semiquinone formation; the solution was bright orange-red when fully reduced, deep violet when fully oxidised, and a deep red-brown at the mid-point.

1 : 5-Dihydroxyanthraquinone (Anthrarufin).—A sample of laboratory reagent quality was resublimed. Both in water and in 50 % pyridine the curves obtained were slightly steeper than corresponded with a simple two-electron oxidation, and they yielded concordant values for \sqrt{K} . There was no visual evidence of semiquinone formation; thus in 50 % pyridine the reduced solution was golden-yellow, when fully oxidised it became dull brown, and from about the mid-point onwards it was a deep red-brown.

1 : 8-Dihydroxyanthraquinone (Chrysazin).—A sample of laboratory reagent quality was resublimed. The curves obtained from titrations both in water and in 50 % pyridine, but especially in the latter, were slightly steeper than corresponded with a two-electron process and they yielded concordant values for \sqrt{K} . There was no visual evidence of semiquinone formation.

Summary.

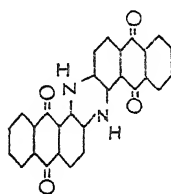
The shapes of the redox titration curves show that semiquinones are formed as intermediate products when the leuco-compounds of many vat dyes are oxidised in alkaline solutions containing pyridine. In the absence of pyridine the only indications of semiquinone formation are the colour changes observed during the oxidative titrations of the vats of certain dyes; nevertheless, it is considered probable that the formation of these intermediate products is general, although the amounts formed must usually be small. The normal potentials of unsubstituted carbocyclic quinones are shown to be related to the numbers of resonating structures of the quinone and the corresponding hydroquinone. Leuco-pyranthrone requires only two equivalents of an oxidising agent for re-oxidation to pyranthrone instead of four equivalents as is required by the constitution given to it by Scholl; a revised constitution is proposed.

II.—THE CONSTITUTIONS OF INDANTHRONE AND OTHER DIQUINONES AND OF THEIR REDUCTION PRODUCTS.

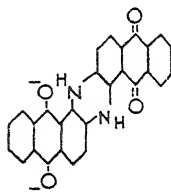
BY DORIS APPLETON AND A. GEAKE.

Received 14th October, 1940.

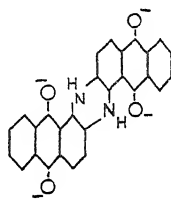
The well-known vat dye indanthrone, formula I, contains two anthraquinone nuclei in the molecule and is, therefore, a diquinone. Reduction with sodium hydrosulphite and sodium hydroxide as in technical dyeing practice occurs to the extent of two equivalents per mole, and yields a blue vat. The resulting hydroquinone ion is usually formulated as II. More drastic reduction leads to the brown, fully-reduced vat containing the hydroquinone ion, III, in which reduction has occurred to the extent of four equivalents per mole. Oxidative titrations have been made with the blue vat in 50 % pyridine (the pyridine delays the



(I)



(II)

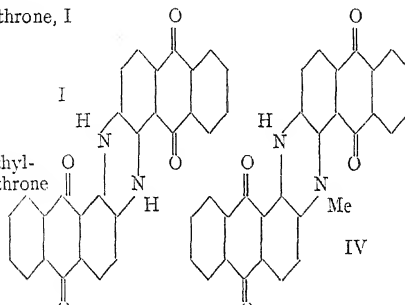
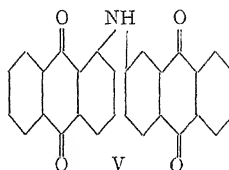
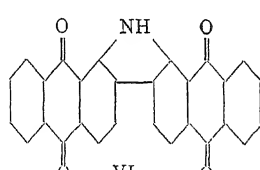
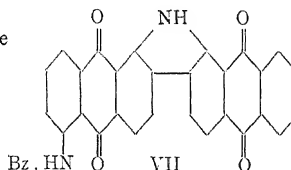
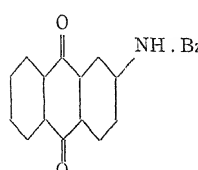


(III)

precipitation of the diquinone) at 50° and the normal potential is -292 mv. Titration of the brown vat has not been possible on account of the very low potential at which it is oxidised, but the conclusion is drawn that the normal potential of its oxidation to the blue vat cannot be above -700 mv. There is, thus, a difference of at least 400 mv. between the two normal potentials. The constitution II for the blue vat implies that, starting from the brown vat one anthrahydroquinone nucleus is oxidised at a normal potential of $\gtrsim -700$ mv., but that the oxidation of the second nucleus then requires a potential at least 400 mv. higher. The brown leuco-compound is symmetrical, and the two anthrahydroquinone nuclei are similar and similarly situated in the molecule. The only difference between the nuclei, when each of them is in turn oxidised, is that the first (normal potential $\gtrsim -700$ mv.) is attached through the nitrogen bridges to an anthrahydroquinone nucleus, whereas the second (normal potential -292 mv.) is attached to an anthraquinone nucleus. This small difference is insufficient to account for so large a difference in normal potential. Thus the difference is much larger than the change in the normal potential of anthraquinone produced by the substitution directly in the nucleus of two benzoylamino or hydroxyl groups. It is the purpose of this paper to suggest that the blue vat is better represented as a resonance hybrid of a number of structures, of which II is one, and it is an essential feature of such a resonance hybrid that it is symmetrical with regard to the two anthraquinone nuclei; it is

TABLE I.

NORMAL POTENTIALS OF DIQUINONES IN 50 PER CENT. PYRIDINE AT 50°.

Substance.	One-electron Normal Potentials.				Two-electron Normal Potentials.	
	E_1 mv.	E_2 mv.	E_3 mv.	E_4 mv.	E_A mv.	E_B mv.
Indanthrone, I	—	—	—	—	—	-292
 I N-Methyl-indanthrone IV.	-664	-698	ca. -454	—	-681	—
1:2'-Dianthrime, V.	-688	-622	-500	-374	-655	-437
 V						
1:1'-Dianthrime carbazole, VI	-704	-646	-435	-373	-675	-404
 VI						
5-Benzoylamino-1:1'-dianthrime carbazole, VII	-687	-625	—	—	-676	—
 Bz. HN VII						
2-Benzoylamino-anthraquinone, VIII	-595	-457	—	—	-526	—
 NH. Bz VIII						

suggested that other anthraquinone vat dyes which are diquinones form similar resonance hybrids when reduced to the extent of two equivalents.

Table I gives data for several diquinones which have been titrated. For all of these, except indanthrone, it was possible to titrate the fully reduced vats, corresponding with reduction by four equivalents, and in all cases the oxidation titration curves had large central potential breaks corresponding with re-oxidation by two equivalents. The first half of each curve was sigmoid in form, and could be analysed¹ into two one-electron curves with the normal potentials E_1 and E_2 . The second halves were also sigmoid until the precipitation of the diquinones began, and when this did not occur too early the two one-electron normal potentials, E_3 and E_4 , could be evaluated. The mid-point potentials of the two halves gave the values of the two-electron normal potentials, E_A and E_B , corresponding with the direct oxidation of the fully reduced dihydroquinone to the product of half oxidation and of this to the fully oxidised diquinone. These are related to the one-electron normal potentials by the equations:

$$E_A = (E_1 + E_2)/2 \quad \text{and} \quad E_B = (E_3 + E_4)/2.$$

The magnitudes of the central breaks are indicated by the differences between E_3 and E_2 . No values of E_3 , E_4 and E_B were obtained for 5-benzoylamino-1:1'-dianthrimide carbazole because precipitation began

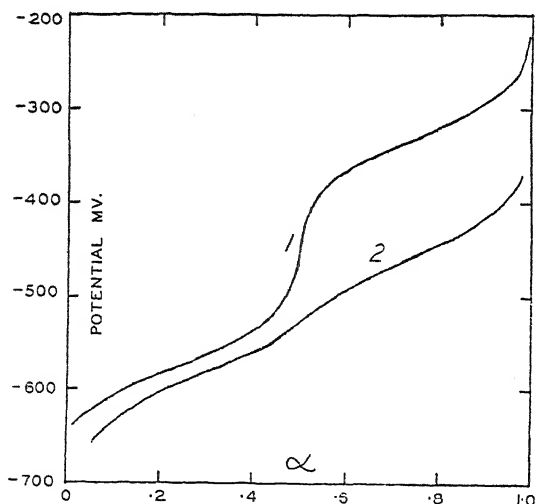


FIG. 1.—1. 1-Benzoylaminoanthraquinone.
2. 2-Benzoylaminoanthraquinone.

soon after the mid-point of the titration, but the curve showed a large central potential break. Of the five diquinones listed in the table, only indanthrone and 1:1'-dianthrimide carbazole are perfectly symmetrical, and the lack of symmetry in the other three substances might contribute to the large central breaks, since the two anthraquinone nuclei are not identical. Nevertheless, comparison of the data for the five dyes shows that the large break is a

characteristic feature of diquinones, and is not dependent on the lack of symmetry of individual dyes.

The simplest of the diquinones listed in the table is 1:2'-dianthrimide. One nucleus in this dye closely resembles 1-benzoylaminoanthraquinone, the vat of which has already been titrated,² the only difference in the

¹ Geake, *Shirley Inst. Mem.*, 1937-38, 16, 111-124, or *Trans. Faraday Soc.*, 1938, 34, 1395-1409.

² Geake and Lemon, *Shirley Inst. Mem.*, 1937-38, 16, 125-142; or *Trans. Faraday Soc.*, 1938, 34, 1409-1427.

vatted state being that the benzoyl group in the latter is replaced in the former by an anthrahydroquinone nucleus. Similarly, the other nucleus resembles 2-benzoylaminoanthraquinone, which has been titrated for comparison with it, and the data for which are included in Table I. The curves for the individual benzoylamino-derivatives are shown in Fig. 1. It is seen that each curve is two-stepped with a definite central potential break, corresponding with the formation of a stable semiquinone. Fig. 2 shows the calculated

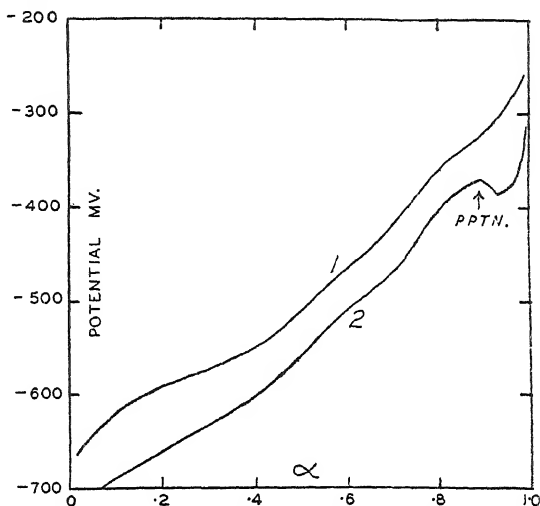
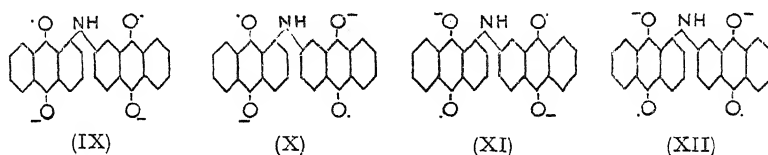


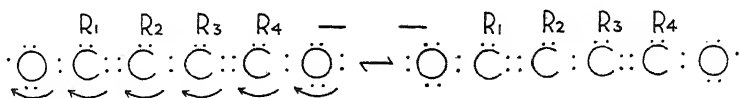
FIG. 2.—1. 1- and 2-Benzoylaminoanthraquinones.
2. 1:2'-Dianthrime.

nucleus was oxidised to the semiquinone stage, and, during the second half, from the semiquinone to the quinone stage. According to this simple view, the stable product of oxidation by two equivalents is a disemiquinone.

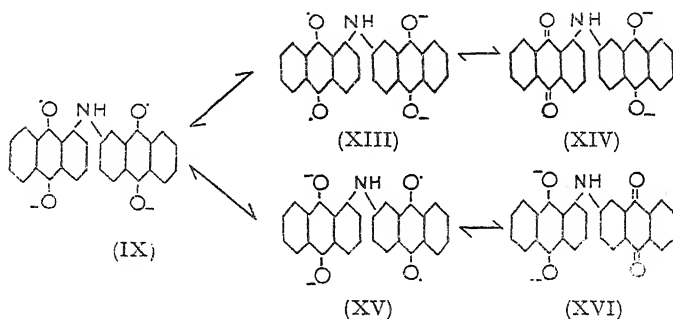
The stability of semiquinones is believed by Pauling and by Michaelis to be due to the extra resonance possible through the unpaired electron being alternatively on either of the two oxygen atoms. Disemiquinones may gain some additional stability through resonance between structures of the following four types:



The dots signify the unpaired electrons. This is not the whole of the resonance which is possible. The type of electronic change which results in the position of the unpaired electron changing from one oxygen atom to the other in the same anthraquinone nucleus, namely :



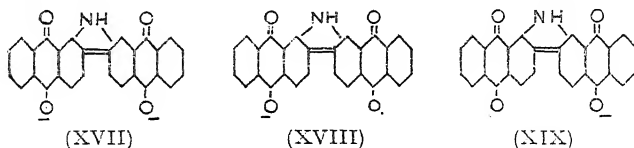
is not dependent on the conjugation of the connecting chain. It should, therefore, be capable of taking place along any chain of carbon and nitrogen atoms, and in consequence of enabling the position of the unpaired electrons to change from one nucleus to the other. By this mechanism each of the two possible mixed hydroquinone-quinone structures, XIV and XVI, can be obtained from any of the structures IX-XII. Thus:



The constitutions of the substances present at the mid-points of the titrations may, therefore, be better represented as resonance hybrids of structures such as IX-XII, XIV and XVI than as simple hydroquinone-quinones such as II (p. 60). It is to be noted that according to the resonance view, both the anthraquinone nuclei are in the same state of oxidation, and no question can arise as to why one nucleus should be oxidised at a lower potential than the other. Kekulé resonance is possible within each of these structures, and each has in fact sixteen Kekulé forms. The total number of resonating structures is thus very large.

The same idea can be applied to the constitutions of the other oxidation products of these vats. Resonance of the type represented by the structures IX to XVI, which may be termed semiquinonoid resonance, is not possible for the fully reduced vats or for the fully oxidised diquinones. The first oxidation product has four resonating structures, corresponding with each of the four oxygen atoms being in turn oxidised and carrying an unpaired electron. The third oxidation product similarly has four structures, corresponding with each of the four oxygen atoms remaining in turn unoxidised and carrying a negative charge; the other oxygen atom in the same nucleus carries an unpaired electron, and the other nucleus is quinonoid. In each of these oxidation products, also, the two anthraquinone nuclei are in the same state of oxidation, and each of the structures referred to can resonate between sixteen Kekulé forms.

The above considerations, which have been illustrated for the case of 1:2'-dianthrime, apply also to indanthrone and its N-methyl deriva-



tive. The carbazoles differ from these substances in that the carbazole bridge renders the two nuclei parts of one conjugated system, and some

additional structures are possible. One additional structure, XVII, is possible for the product present at the mid-point; this is free from unpaired electrons but has only four Kekulé forms. Two additional structures, XVIII and XIX, are possible for the third oxidation product, but each of these, also, exists in only four Kekulé forms.

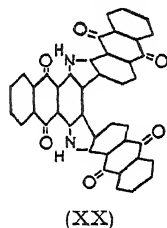
Thus, if only semiquinonoid resonance is considered, and structures such as XIII are disregarded, the following are the numbers of resonating structures at the various stages of oxidation of the vats of diquinones:—

TABLE II.

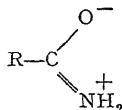
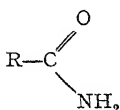
Equivalents of oxidation	O	1	2	3	4
No. of structures { Anthrimides and indanthrones	1	4	6	4	1
{ Carbazoles	1	4	7	6	1

The second oxidation products are stable, corresponding with the large central potential breaks, not only because the number of structures is the largest but also because some of these structures are free from unpaired electrons, whereas all the structures of the products of their one-electron oxidation and reduction contain this element of instability.

The behaviour of the triquinone 1:2:3:4:1':2':1'':2''-tri-anthrimide dicarbazole, XX, agrees with the course of oxidation postulated for the diquinones. The first half of the titration, corresponding with the addition of three equivalents of the oxidising agent, yielded a complex sigmoid curve; there was a large potential break at the midpoint followed almost immediately by the beginning of precipitation. This behaviour could hardly be explained on the assumption that each of the three anthrahydroquinone nuclei was oxidised in turn.

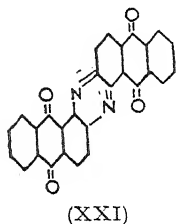


It is evident that other kinds of resonance besides those considered must be possible for many of the substances which have been discussed. Such resonances are those characteristic of phenol, aniline, quinone and amides; also hydrogen bonding may occur between imino-groups and carbonyl or hydroxyl groups. The first three resonances and hydrogen bonding have small energies compared with amide resonance and with Kekulé resonance. The total of such minor effects may, however, well be important. It has been shown already that the inclusion of Kekulé



resonance greatly increases the absolute numbers of structures but has little effect on the relative numbers of structures of the various oxidation products; it is these relative numbers that are likely to be related to values of the normal potentials. The inclusion of amide resonance, as well as of Kekulé resonance, also has only a small effect on the relative numbers of structures at different stages of oxidation of anthrimides and carbazoles, and in particular the number still increases to a maximum at the second oxidation product. For indanthrones the maximum is shifted to the third oxidation product, but although the second oxidation product has rather fewer structures than the third, it still has the advantage that many of these are free from unpaired electrons. No amide resonance is possible for the fully reduced dihydroquinones as

these contain no carbonyl groups. For the fully oxidised diquinones of anthrimides and carbazoles two additional structures are possible, each with a number of Kekulé forms. For indanthrone, with its two imino-groups, many additional structures are possible, and when both Kekulé and amide resonances are considered, indanthrone is viewed as a resonance hybrid of 96 structures. This provides a reason for the great ease with which anthraquinoneazine, XXI, for which amide resonance is not possible, is reduced to indanthrone.



Experimental.

The general procedure used in making the titrations has been described already.² All the dyes referred to in this paper were titrated both in aqueous 0.1 N sodium hydroxide, 0.09 M in sodium sulphate, and in 50 % pyridine 0.1 N in sodium hydroxide. The dyes were so insoluble that normal potentials could seldom be evaluated from the data obtained in aqueous solutions, and the normal potentials given above were all obtained in 50 % pyridine. The oxidising agent used was generally phenol indo-2 : 6-dichlorophenol, which has a lower normal potential, and is, therefore, milder in its action, than potassium ferricyanide, which was used when the potential of the indophenol was too low. All the titrations were made at 50°.

Indanthrone.—The material used was a commercial sample recrystallised three times from 1000 parts of quinoline. Even in 50 % pyridine the oxidised dye was so insoluble that precipitation began very early when the blue vat was titrated at a concentration of 1 m. mol./l., and it was only at the extreme dilution of 2×10^{-2} m. mol./l. that precipitation was sufficiently delayed for values of the normal potential to be obtained from the first, sigmoid, part of the curve. The use of this high dilution somewhat diminished the accuracy of the data, but several titrations agreed in giving curves that did not depart significantly from the form calculated for a two-electron oxidation and in yielding values close to -292 mv. for the two-electron normal potential; there was thus no evidence for the formation of an intermediate product. The brown vat could be obtained by more drastic reduction, for example, by raising the temperature, but no satisfactory titration curves could be obtained.

N-Methylindanthrone.—The material titrated was a sample of Indanthrene Blue RK which is stated by Rowe³ to have this constitution; it was recrystallised from nitrobenzene. The normal vatting procedure resulted in the brown vat, and no difficulty was experienced in its titration. In 50 % pyridine, at a concentration of 0.5 m. mol./l., precipitation began shortly after the mid-point, corresponding with the addition of two equivalents of the oxidising agent. The first half of the titration yielded a sigmoid curve ($\sqrt{K^*} = 0.6$), and during this time the colour changed from brown to green, the colour of the intermediate vat in 50 % pyridine. When the concentration was halved, precipitation still occurred before the mid-point of the second half of the titration. The early points on this half of the curve yielded concordant values for the normal potential when a one-electron process was assumed, but drifting values for a two-electron normal potential. There was thus qualitative evidence of semiquinone formation at this stage, and an approximate value of the one-electron normal potential, namely, -454 mv., was obtained. When titrated in water at a concentration of 0.5 m. mol./l., precipitation began when the whole oxidation was

³ Rowe, *The Development of the Chemistry of Commercial Synthetic Dyes* (1856-1938), Institute of Chemistry Monograph, 1938.

* K is the formation constant of the semiquinone.

about 20 % complete, and there was, therefore, appreciable separation of the two main stages of the oxidation.

1 : 2'-Dianthrime.—The sample used was synthesised from purified intermediates, and was recrystallised. At a concentration of 0.5 m. mol./l. in 50 % pyridine precipitation began shortly after the mid-point, and only the first two one-electron normal potentials could be evaluated. At one-tenth of this concentration all four normal potentials were obtained. The values found for \sqrt{K} at the first and second stages of the oxidation were 3.2 and 9.7 respectively.

1 : 1'-Dianthrime carbazole.—Indanthrene Yellow FFRK, which is stated to have this composition,³ was recrystallised three times from 500 parts of nitrobenzene. At a concentration of 0.5 m. mol./l. in 50 % pyridine precipitation began very soon after the mid-point, but the curve for the first half of the titration was sigmoid, giving $\sqrt{K} = 2.9$. Normal potentials for the second half of the oxidation were obtained at a concentration of 0.04 m. mol./l. and the value found for \sqrt{K} at this stage of the oxidation was 3.1.

5-Benzoylamino-1 : 1'-dianthrime carbazole.—This was recrystallised twice from 1000 parts of nitrobenzene. When titrated in 50 % pyridine at a concentration of 0.5 m. mol./l. the first half of the oxidation yielded a sigmoid titration curve ($\sqrt{K} = 3.0$), and precipitation began shortly after the mid-point.

1 : 2 : 3 : 4 : 1' : 2' : 1'' : 2''-Trianthrime dicarbazole.—Indanthrene Brown BR is stated to have this composition.⁴ The dye is so insoluble that no solvent was found from which it could be recrystallised. To remove more soluble substances it was boiled twice with 1000 parts of quinoline, filtered at the boil, and the undissolved residue, which amounted to 50 % of the whole, was used for titrations. When titrated in 50 % pyridine at concentrations of 0.3 and 0.03 m. mol./l., the first halves of the curves were sigmoid, but precipitation began shortly after the mid-point. The steepness of the sigmoid curve showed that it was built up from one-electron curves corresponding with different normal potentials. The curves did not appear sufficiently accurate, probably on account of impurities in the dye, to attempt the analysis of this unusually complex case.

2-Benzoylaminoanthraquinone.—A recrystallised sample was titrated in 50 % pyridine for comparison with 1 : 2'-dianthrime, and no precipitation occurred at a concentration of 1 m. mol./l. The curve was two-stepped, and gave concordant values for \sqrt{K} , the mean being 11.8. This value is lower than that for anthraquinone (25.2), whereas that for 1-benzoylaminoanthraquinone is higher (83).² When the vat was titrated in water precipitation began early, but the points on the short branch of the curve which preceded precipitation gave concordant values for the normal potential when a one-electron process was assumed, but drifting values for the normal potential of a two-electron process. There is, therefore, qualitative evidence that a semiquinone is formed in water.

Summary.

It is suggested that indanthrone and other vat dyes containing two anthraquinone nuclei in the molecule, as well as the reduction products of these dyes, are resonance hybrids, so that in each of these substances the two nuclei are in the same state of oxidation. The most important types of resonance are that postulated by Pauling and by Michaelis for semiquinones, and the Kekulé resonance. The vats of these dyes can usually be oxidised in four stages, corresponding with the four oxidisable phenolic groups, and there are, thus, three intermediate oxidation products; all of these are more or less semiquinonoid in character.

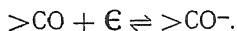
⁴ Thomson, *J. Soc. Dyers and Col.*, 1936, 52, 237-247.

III.—THE OXIDATION AND REDUCTION OF ANTHRAQUINONOID VAT DYES IN CONCENTRATED SULPHURIC ACID.

By A. GEAKE.

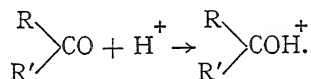
Received 14th October, 1940.

It has been shown¹ that the reduction of an anthraquinonoid vat dye in an alkaline medium is an electrochemically reversible process in which the potential-determining reactants are presumed to be the undissociated quinone and the anion of the hydroquinone or the semi-quinone. For each reactive carbonyl group in the molecule the redox equilibrium may be represented:

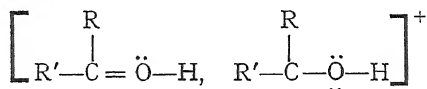


The concentration of the oxidised form in any aqueous alkaline solution is extremely low, the vat dyes being highly insoluble in water.

Most anthraquinonoid vat dyes are readily soluble in concentrated sulphuric acid (> 85 %) and such solutions have characteristic colours generally very different from the colours of the solid dyes or of their solutions in organic solvents. This may be attributed to the basic ionisation of the quinone in the strongly acid medium:

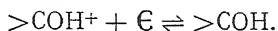


The resulting ion is believed to be a resonance hybrid of oxonium and carbonium ion structures:



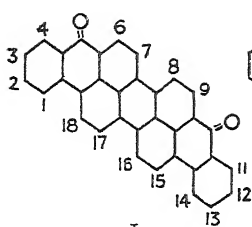
and it may be termed a quinonium ion.

Qualitative experiments show that the addition of a strong reducing agent, such as chromous sulphate, to the sulphuric acid solutions of some anthraquinonoid vat dyes causes a colour change which can be reversed by the addition of an oxidising agent. It is to be presumed that the colours correspond to the quinone and hydroquinone redox stages, and the reactions involved might be represented as electrochemically reversible processes involving the gain of an electron by the quinonium ion to form the undissociated hydroquinone:

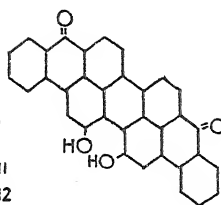


One of the objects of the work to be described was to determine, by the method of redox titration, whether the existence of such an electrochemical equilibrium could be demonstrated experimentally.

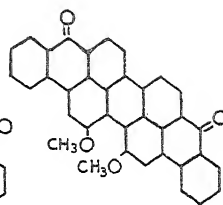
¹ Geake and Lemon, *Shirley Inst. Mem.*, 1937-38, 16, 125-142, or *Trans. Faraday Soc.*, 1938, 34, 1409-1427; Appleton and Geake, two preceding papers.



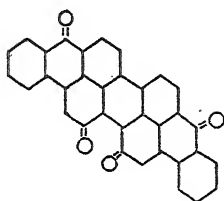
I



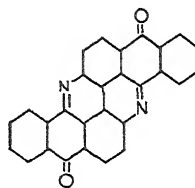
II



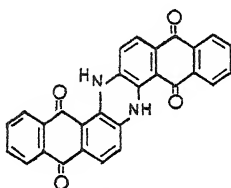
III



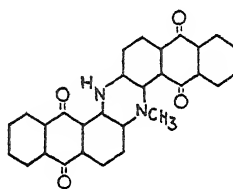
IV



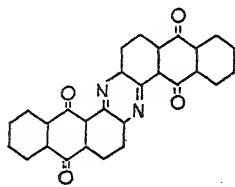
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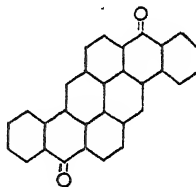
VI



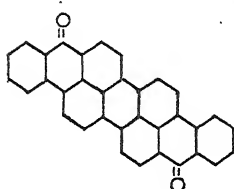
VII



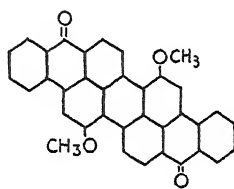
VIII



IX



X



XI

- | | | | |
|-----|-------------------------------|------|---------------------------------|
| I | Dibenanthrone. | VI | Indanthrone. |
| II | 16:17-Dihydroxydibenanthrone. | VII | N-Methylindanthrone. |
| III | 16:17-Dimethoxydibenanthrone. | VIII | Anthraquinoneazine. |
| IV | 16:17-Diketodibenanthrone. | IX | Pyranthrene. |
| V | Flavanthrene. | X | iso-Dibenanthrone. |
| | | XI | 8:17-Dimethoxyisodibenanthrone. |

Further qualitative experiments have shown that the great majority of anthraquinonoid vat dyes experience colour changes on the addition of a strong *oxidising* agent, such as ceric sulphate, and these changes are often more or less perfectly reversed by the addition of a reducing agent. One of the most striking examples of this behaviour has already been reported by Thomson² and occurs with 16:17-dimethoxydibenzanthrone (III, Caledon Jade Green). The solution of this green dye in concentrated sulphuric acid is of a magenta colour, changing to a brilliant green on the addition of ceric sulphate or other strong oxidising agent; the addition of a reducing agent reverses this change. Unsubstituted dibenzanthrone (I) and other derivatives believed to be substituted in the 16 and 17 positions also dissolve in concentrated sulphuric acid to yield reddish solutions which can be oxidised to green. The 16:17-dihydroxy-derivative (II) is, however, exceptional, since, although it shows a perfectly reversible colour change with ceric sulphate, the change is from red to brown on oxidation, and not from red to green as with other dibenzanthrone derivatives. Examples of other reversible colour changes are: isodibenzanthrone (X), bright green to violet; indanthrone (VI), yellowish-brown to red, and similar changes for substituted indanthrones; pyranthrene (IX), deep reddish-blue to a duller shade, etc. In a number of these cases the apparently perfect and instantaneous reversibility of the colour change suggests that the processes are purely electronic, but no attempt has so far been made to formulate them. Thomson² observed that when the magenta solution of Caledon Jade Green (III) in sulphuric acid is poured into water the dye is recovered unchanged, but that when the green solution, obtained from it by oxidation, is diluted the precipitate contains 16:17-diketo-dibenzanthrone (IV). The formation of this compound involves dealkylation of the dye, and such a process cannot account for the instantaneously reversible colour change. As was realised by Thomson, the formation of the diketo-compound must occur during the dilution of the green oxidised solution, and not during the oxidation of the magenta to the green.

The second object of the work described here was to determine, by the method of redox titrations, whether the oxidation of anthraquinonoid vat dyes dissolved in sulphuric acid occurs in an electrochemically reversible manner, and if so, to suggest a mechanism for the redox processes involved.

For the redox titration of concentrated sulphuric acid solutions the choice of a suitable comparison half-cell presents some difficulty, since half-cells containing dilute aqueous electrolyte solutions must be expected to give large and variable liquid junction potentials. The half-cell finally adopted consisted of a platinum wire dipping in 88.4 % (1600 g./l.) sulphuric acid 0.005 M in ferrous and ferric iron and out of contact with the air. This solution must be freshly made each day, since it deposits a ferric compound on longer standing. The half-cell is reproducible, and titrations made in the same concentration of sulphuric acid can therefore be compared. Potentials measured in different concentrations of sulphuric acid are not comparable on account of unknown differences in liquid junction potential. The potential of the half-cell is not known, and in deriving the electrode potentials recorded in this paper it is arbitrarily assumed to be zero. All titrations were made with 0.05 M molar solutions of the dyes at 20°, the oxidation titrations with 0.1 N ceric sulphate in 5 N

² Thomson, *J. Soc. Dyers and Col.*, 1936, 52, 251.

sulphuric acid, and the reduction titrations with 0.1 N neutral chromous sulphate, or, in a few cases, with 0.1 N titanous sulphate in 5 N sulphuric acid. The volume of titrating solution added was generally less than 1 % of that of the titrated dye solution, so that the change in sulphuric acid concentration during a titration was only small.

Most of the dyes used were specially purified for this work. The substance described as N-methylindanthrone was a recrystallised sample of Indanthrene Blue RK, to which this structure is attributed by Rowe.³

Reduction Titrations.

Of the anthraquinonoid vat dyes examined, only flavanthrone (V), indanthrone (VI) and N-methylindanthrone (VII) yielded reasonably well-defined potentials in reduction titrations and gave the sigmoid type of titration curve characteristic of simple electron exchange processes.* Fig. 1 shows

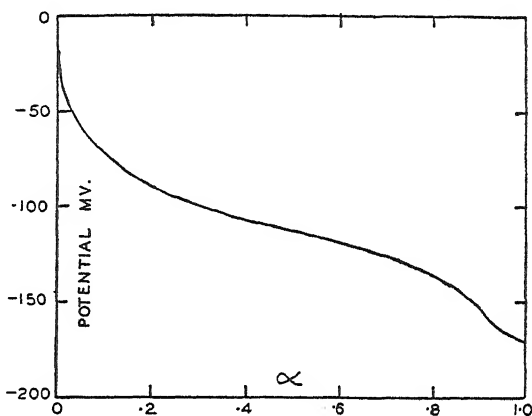


FIG. 1.

a reduction curve for flavanthrone in 90 % sulphuric acid solution, a concentration at which better results were obtained than with more concentrated acid. The reversibility of the process was checked by several titrations in which flavanthrone was first reduced with chromous sulphate in the absence of air and then re-oxidised with ceric sulphate. Both reduction and re-oxidation required two equivalents per mole of dye, and the values of fractional reduction (α) are plotted as abscissæ in Fig. 1. The form of the curve is close to that of a two-electron process, but all titrations agreed in giving curves for which the slopes were slightly greater than the calculated value. The conclusion must be drawn that the reduction of flavanthrone in sulphuric acid proceeds in two overlapping one-electron stages with the formation of an intermediate product. If K is the formation constant of this intermediate product, defined by the relation

$$K = \frac{[\text{Intermediate product}]^2}{[\text{Fully oxidised product}][\text{Fully reduced product}]}$$

the mean value of \sqrt{K} obtained from the titration curves by methods already described⁴ was 0.4.

In order to confirm the reality of the formation of an intermediate product the spectrum of a partly reduced solution was compared with those of fully oxidised and fully reduced solutions of the same total

³ Rowe, *The Development of the Chemistry of the Commercial Synthetic Dyes* (1856-1938); Institute of Chemistry Monograph, 1938.

* Indigo also gives a sigmoid reduction curve.

⁴ Geake, *Shirley Inst. Mem.*, 1937-38, 16, 111-124, or *Trans. Faraday Soc.*, 1938, 34, 1395-1409.

concentration. The spectral curves are shown in Fig. 2; it is seen that the curve for the partly reduced solution passes above the isobestic point at $542\text{ m}\mu$, indicating the presence of a small proportion of an absorbing substance other than the two end products. A minimum value of \sqrt{K} , found to be 0.2, could be calculated on the assumptions that the whole of the absorption of the partly reduced solution at $703\text{ m}\mu$ was due to the fully reduced form, that the whole of the absorption at $507\text{ m}\mu$ was due to the fully reduced and fully oxidised forms, and that Beer's law was applicable.

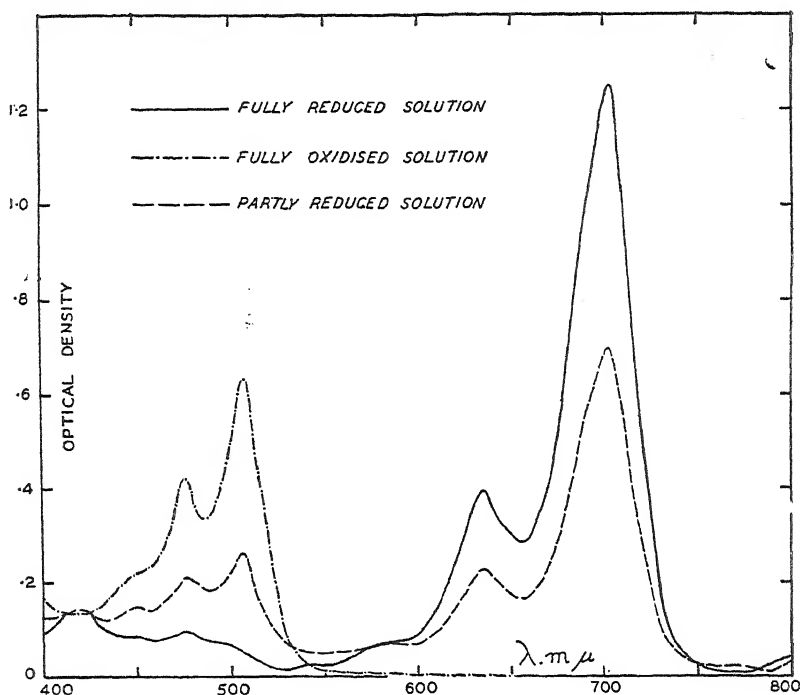


FIG. 2.

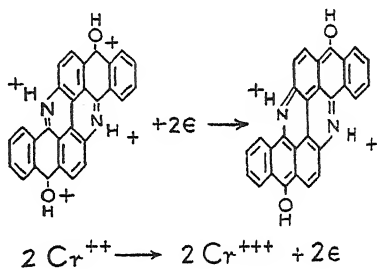
Reversible titration curves were also obtained by the reduction of indanthrone and N-methylindanthrone in 90 % sulphuric acid. The titres again corresponded with two equivalents per mole of dye, and the slopes of the curves were equal to, or slightly greater than, that calculated for a two-electron process. The normal potentials obtained, which are not very accurately defined, are given below:—

	Normal potential.	Colour change on reduction.
Flavanthrone	—115 mv.	Orange to bright green.
Indanthrone	—298 mv.	Yellow-brown to red-brown.
N-Methylindanthrone ..	—317 mv.	Green-brown to red-brown.

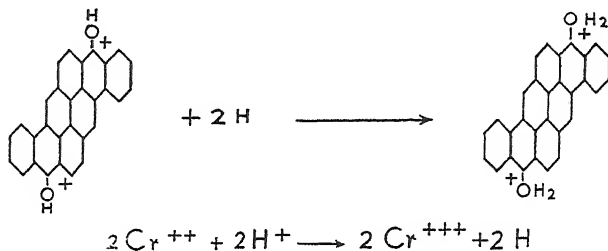
Flavanthrone is seen to be reduced at a much higher potential than indanthrone, and this is true also for the reduction of these dyes in alkaline solutions.

When many other vat dyes were titrated with chromous sulphate, for example dibenzanthrone and its derivatives, no definite potentials were obtained, and duplicate platinum electrodes in the titration vessel registered different potentials, in spite of the fact that reversible colour changes occurred. Thus the addition of chromous sulphate to a solution of dibenzanthrone in sulphuric acid changes the colour from magenta to blue-violet. Since a blue-violet solution also results from the dissolution in sulphuric acid of the acid leuco-compound of dibenzanthrone, obtained by reduction in an alkaline solution and acidification, it seems probable that reduction of dibenzanthrone to the corresponding hydroquinone actually occurs when its sulphuric acid solution is treated with chromous sulphate. The process does not, however, define the potential at a platinum electrode.

The difference between flavanthrone or indanthrone, whose reductions show the characteristics of simple electron exchange processes, and dibenzanthrone or pyranthrone, for which this is not the case, may be associated with the fact that the former, unlike the latter, are heterocyclic quinones containing nitrogen. No information is available regarding the ionisation in concentrated sulphuric acid of any of these dyes, but the following suggestions give a possible explanation of the experimental observations. It is assumed that in the nitrogenous dyes both the nitrogen atoms and the carbonyl groups are ionised, and that reduction consists in the gain of two electrons leading to hydroquinones ionised at the nitrogen atoms only. This is the kind of potential-determining system postulated at the beginning of the paper; thus for flavanthrone.



Dyes such as dibenzanthrone and pyranthrone are homocyclic quinones containing only carbon, hydrogen and oxygen. The solubility of their leuco-compounds in sulphuric acid suggests that these are ionised and this can only be at the hydroxyl groups. The reduction of the quinone is then represented by the scheme (for pyranthrone) :



According to this formulation the reduction of the dye does not consist of an electron gain, and for this reason the process could not be expected to control the potential of an inert electrode. The absence of ionisation at the hydroxyl groups in the leuco-compounds of the nitrogenous dyes might be due to the ionisation at the nitrogen atoms preventing further ionisation.

Oxidation Titrations.

Fig. 3 shows the titration curves obtained with ceric sulphate for 0.05 m.molar solutions of 16:17-dimethoxydibenzanthrone in 97.3 % and 88.4 % sulphuric acid. Two equivalents

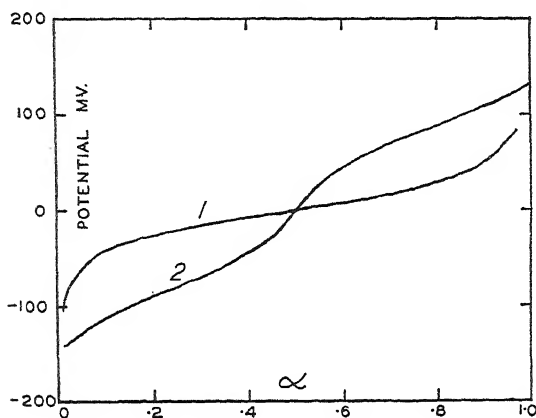


FIG. 3.—1. 88.4 % H_2SO_4 .
2. 97.3 % H_2SO_4 .

of the oxidising agent were consumed per mole of dye, and values of fractional oxidation are plotted as abscissae. Since the absolute values of the potentials measured for the two different concentrations of sulphuric acid are not comparable, the ordinates plotted are the differences between the potentials at the mid-points of the titrations and the potentials at other values

of the fractional oxidation. The curve obtained in the higher concentration of acid consists of two steps, and shows that an intermediate product of considerable stability is formed; the points throughout the curve yield concordant values for \sqrt{K} with a mean of 23.4. The curve obtained in 88.4 % acid does not contain two steps, but analysis shows that it represents two overlapping one-electron processes, and concordant values of \sqrt{K} were obtained with a mean of 0.96. Oxidised solutions obtained in the higher concentration of sulphuric acid were back-titrated with titanous sulphate and ferrous ammonium sulphate. The curves were reversible approximately as far as the

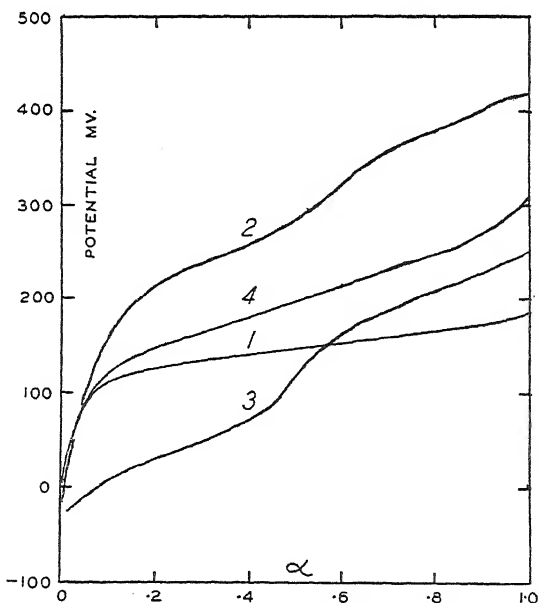


FIG. 4.—1. Dihydroxydibenzanthrone.
2. Dihydroxydibenzanthrone ethylene ether.
3. Dimethoxydibenzanthrone.
4. Dimethoxyisodibenzanthrone.

mid-point, but these reducing agents appeared to be insufficiently powerful to bring the potential back to its initial low value. There was little colour change during the first half of the oxidation, the change from magenta to green occurring during the second half.

Fig. 4 (Curve 1) shows the titration curve obtained with ceric sulphate for a 0.05 m.molar solution of 16 : 17-dihydroxydibenzanthrone (II) in 98 % sulphuric acid. Compared with it are the curves obtained in the same medium with the ethylene ether of this compound (curve 2), and with the dimethyl ether (curve 3) for which the results have already been discussed and illustrated in Fig. 3; curve 4 in Fig. 4 shows the results obtained with Caledon Ming Blue X.* In all these cases characteristic sigmoid curves were obtained, but the end-points were generally not sharp, and no final rapid rises of potential occurred to the high values expected for the ceric-cerous system. This is believed to be due to irreversible oxidation processes becoming progressively more important as the potential rises towards the ends of the titrations. Back titration with titanous sulphate produced reversals of the colour changes, and more or less perfect reversals of the potential curves. In spite of the lack of sharp end-points there could be no doubt that the reversible oxidation processes consumed two equivalents of oxidising agent per mole of dye, and the values of fractional oxidation plotted in Fig. 4 were calculated on this assumption. Since all the titrations represented in this figure were carried out in the same concentration of sulphuric acid, the potentials plotted are those actually measured. Analysis of the curves showed that in every case the oxidation process occurred in two one-electron stages; the following are the values of the constants:—

	Normal potential.	\sqrt{K} .	Colour change on oxidation.
16 : 17-Dihydroxydibenzanthrone	148 mv.	0.3	Magenta to red-brown.
Dimethyl ether of "	118 mv.	23.4	Magenta to green.
Ethylene ether of "	ca. 320 mv.	ca. 16	Magenta to green.
Caledon Ming Blue X	200 mv.	4.5	Red-brown to magenta

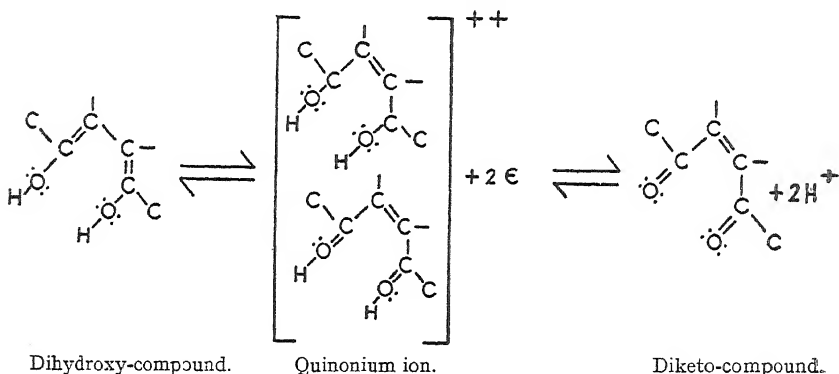
With the last two dyes in the table, which have the highest normal potentials, the titrations were carried out as rapidly as possible to minimise the effect of irreversible oxidation processes; this involved some sacrifice of precision. It will be seen that the formation constant of the intermediate product is much lower for the free dihydroxy-derivative than for the ethers, being only just significantly different from zero.

With many other anthraquinonoid vat dyes examined—for example, the unsubstituted homocyclic quinones dibenzanthrone, *isodibenzanthrone* and pyranthrone—no reversible behaviour was observed in the electrometric titrations. The potential rose during the first additions of ceric sulphate, and then remained roughly constant during the addition of further relatively large quantities of the oxidising agent, though it was not well-defined and drifted downwards with time. In these cases the oxidising agent was consumed in irreversible oxidation processes, and reasonably sharp end-points could eventually be reached at which the potential rose to high values (800 to 900 mv.) corresponding with the presence of an excess of the oxidising agent. These end-points represented consumptions of about 32, 28, and 26 equivalents of

* This is stated by Rowe³ to be 8 : 17-dimethoxyisodibenzanthrone (XI).

oxygen, respectively, per mole of the three quinones mentioned above. For dibenzanthrone and *isodibenzanthrone* they correspond approximately with known oxidations to 2:2'-dianthraquinonyl-1:1'-dicarboxylic acid⁵ and indoquinonanthrene,⁶ respectively, in which parts of the original condensed ring systems have suffered destructive oxidation. In spite of this, all three quinones show reversible colour changes in qualitative test-tube experiments; in particular, a solution of dibenzanthrone in sulphuric acid changes in colour from magenta to green on oxidation, and this change is closely similar to that of its dimethoxy-derivative for which a reversible titration curve can be obtained. The explanation no doubt is that a reversible oxidation occurs in all these cases, and can be detected in the qualitative experiments carried out rapidly with considerable excesses of oxidising and reducing agents, but it is masked by the irreversible reactions in the much slower titration process where no excess of oxidising agent is present. The importance of these observations is that any postulated reaction mechanism for the reversible oxidation must be applicable to the unsubstituted homocyclic quinones, and not only to those derivatives for which the electrochemical reversibility of the oxidation has been experimentally established.

No difficulty presents itself in postulating a reversible oxidation mechanism for 16:17-dihydroxydibenzanthrone (II) since the product of the oxidation is known and can be isolated. It is diketodibenzanthrone (IV). This substance can be prepared by the oxidation of a suspension of the dihydroxy-compound with dichromate in dilute sulphuric acid. When it was dissolved in 98 % sulphuric acid and titrated with a reducing agent, it yielded a curve which almost perfectly reversed the oxidation curve of the dihydroxy-compound shown in Fig. 4 (curve 1). Dihydroxydibenzanthrone can evidently be regarded as a hydroquinone derived from the diketo-compound. In concentrated sulphuric acid solution it is assumed to be ionised at the two quinone groups, and by the loss of two electrons on oxidation to pass into the quinonium ion formed by the ionisation of the diketo-compound at all four carbonyl groups. This is the simple process of electron exchange already postulated to account for the reversible reduction of flavanthrone in sulphuric acid solution. The equilibria in the dihydroxy-diketo-system are represented below, the formulæ showing only the important parts of the molecules in the region of the 16- and 17-carbon atoms:



⁵ Scholl, Müller and Böttger, *Ber. deut. chem. Ges.*, B, 1935, 68, 45-49.

⁶ Scholl and Kurt Meyer, *ibid.*, 1928, 61, 2550-2555.

Of the two resonating structures given above for the quinonium ion one represents it as formed from the dihydroxy-compound by the loss of electrons from a pair of ring carbon atoms, namely, the 16- and 17-carbon atoms, and the other as formed by the loss of electrons from the two oxygen atoms. It has been seen that a similar reversible oxidation must be postulated for unsubstituted dibenzanthrone, although strict electrochemical evidence is not obtainable. For this substance the loss of electrons can occur only at a pair of carbon atoms; these need not necessarily be the 16- and 17-carbon atoms, as several other possible pairs are available, for example, the 1- and 14-carbon atoms. Structures formed by the loss of electrons from different pairs of carbon atoms differ only in the arrangement of the electrons within the molecule, and the oxidation product of dibenzanthrone is therefore likely to be a resonance hybrid of various structures of this type. 16:17-Diamino-dibenzanthrone behaves qualitatively like dibenzanthrone itself in being oxidised from a red to a green solution. When this substance is dissolved in sulphuric acid it must be assumed that the nitrogen atoms are ionised and this makes it improbable that the 16- and 17-carbon atoms, attached to these nitrogen atoms, will be ionised on oxidation. Since the 16:17-dibenzanthrone ethers are also oxidised from red to green it is possible that the ethereal oxygen atoms are ionised and that ionisation of the 16- and 17-carbon atoms is prevented for these substances also. The de-alkylation which occurs when an oxidised solution of dimethoxydibenzanthrone is poured into water might be regarded as evidence that oxidation had occurred at or near the 16- and 17-positions, but any suspension of dimethoxydibenzanthrone in dilute acid is similarly de-alkylated by an oxidising agent. If the above arguments are valid the oxidation products of dibenzanthrone and its derivatives, except the dihydroxy-compound, are to be regarded as resonance hybrids of structures ionised at various pairs of carbon atoms, ionisation at the 16- and 17-carbon atoms playing not more than a small part; by contrast the oxidation product of the dihydroxy-compound which differs in colour from all the other oxidation products, is a resonance hybrid of structures ionised at the 16- and 17-carbon atoms and at the two oxygen atoms, respectively. This difference between the oxidation products of dihydroxydibenzanthrone and the other dibenzanthrone derivatives agrees with the different values found for \sqrt{K} . One structure, the oxonium ion structure, of the oxidation product of the former possesses complete octets round all the carbon and oxygen atoms and this oxidation product is therefore likely to be more stable than those of the other dibenzanthrone derivatives for which all the structures contain two carbon atoms with incomplete octets. Increased stability of the fully oxidised product will tend to diminish the amount of the intermediate product formed and in agreement with this the value of \sqrt{K} found for the dihydroxy-compound, namely, 0.3, is so low as to be of dubious reality, whereas high values, namely, 16 and 23, have been obtained for the dibenzanthrone ethers.

The suggestion that the oxidation process usually consists in the loss of two electrons from a pair of carbon atoms is evidently sufficiently general to be applicable to most anthraquinonoid vat dyes and thus to account for the observed generality of a reversible colour change.

Apart from derivatives of dibenzanthrone and *isodibenzanthrone* the only anthraquinonoid vat dyes for which reversible oxidation titration curves have been obtained in concentrated (98 %) sulphuric acid

are indanthrone (VI), N-methylindanthrone (VII) and trichloroindanthrone. These curves are shown in Fig. 5. Indanthrone and its derivatives contain two anthraquinone nuclei in the molecule but only two equivalents of ceric sulphate are required, as for the dibenzan-

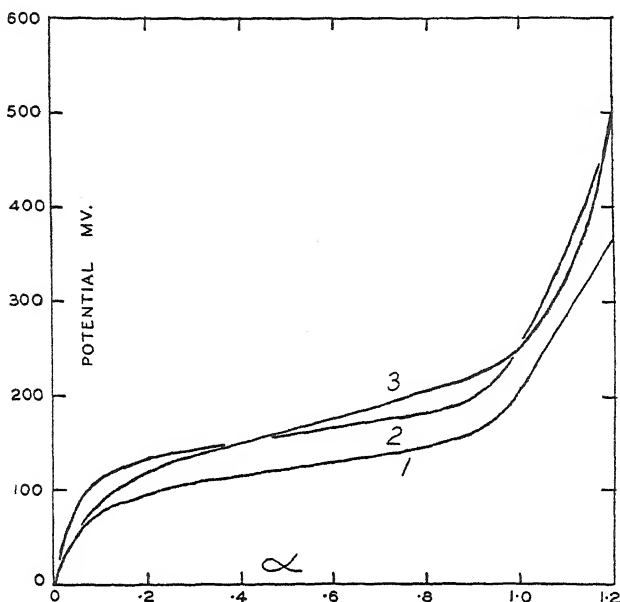


FIG. 5.—1. Indanthrone.
2. N-Methylindanthrone.
3. Trichloroindanthrone.

throne derivatives, which are monoquinones. When an excess of ceric sulphate is added high potentials are obtained with no evidence of a second reversible oxidation process. The constants obtained from the curves and the observed colour changes are as follows :—

	Normal potential.	\sqrt{K} .	Colour change on oxidation.
Indanthrone.	124 mv.	0.7	Yellow-brown to red.
N-Methylindanthrone. . .	161 mv.	0.8	Dull brown to orange-red.
Trichloroindanthrone.* . .	170 mv.	—	Yellow-brown to dull red.

* Unlike all the other substances titrated, this was not specially purified.

The forms of the curves approach closely to that for a two-electron process, the recorded values of \sqrt{K} being only just significantly different from zero. Of the anthraquinonoid vat dyes examined, indanthrone and its derivatives are the only ones which can be both reversibly reduced and reversibly oxidised in titrations in sulphuric acid. If the solution reduced with chromous sulphate is titrated with ceric sulphate the complete oxidation curve thus obtained represents two widely separate two-electron stages, and the colour alters from red brown in the fully

reduced state, through yellow-brown for the solution of indanthrone itself, to red in the oxidised state.

When the oxidised solution of indanthrone in sulphuric acid is poured into water a yellow precipitate is obtained which is probably anthraquinoneazine (VIII). It is, however, improbable that this azine is formed during the actual oxidation in sulphuric acid because N-methylindanthrone, which on account of the methyl group could not form the azine, gives a similar colour change and titration curve. When an oxidised solution of N-methylindanthrone is poured into water a blue precipitate is obtained, evidently because azine formation is not possible. If the oxidation of indanthrone results in the loss of two electrons from a pair of carbon atoms the two atoms must be in the same benzene ring if the ordinary constitution (VI) is accepted, because, according to this constitution, no two benzene rings form parts of the same conjugated system. The constitution of indanthrone has been discussed in the foregoing paper describing the oxidative titration of its vat, where it is shown that this dye is probably best regarded as a resonance hybrid of a large number of structures. In some of these structures the whole molecule is a single conjugated system, and the conclusion may be drawn that electrons may be lost by various pairs of symmetrically arranged carbon atoms.

Summary.

When dissolved in sulphuric acid, certain anthraquinonoid vat dyes are capable of reversible oxidation, reversible reduction, or both. The dyes for which reversible reduction curves have been obtained contain nitrogen, and it is probable that they are reduced to ionised forms of the hydroquinones. It is probable that some other dyes are reversibly reduced, but that the process is not able to control the potential of an inert electrode. It is suggested that reversible oxidation generally leads to products which are resonance hybrids of structures in which two electrons have been lost by various pairs of carbon atoms. Many dyes that give reversible colour changes with an oxidising agent do not give sigmoid titration curves. This is probably because, in the relatively slow titrations, the rapid reversible oxidation processes are masked by slower irreversible destructive oxidations.

The authors of this and the two foregoing papers are indebted to Messrs. Imperial Chemical Industries, Ltd., who provided samples of many dyes and related substances specially prepared for the work.

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Shirley Institute, Didsbury, Manchester.*

REVIEWS OF BOOKS.

Surface Tension and the Spreading of Liquids. By R. S. BURDON.
Cambridge Physical Tracts. Pp. 85 + xii. Price 7s. 6d. net.

This book presents, very clearly and directly, the essential facts and theories concerned in surface tension, its measurement, and the spreading of liquids on liquids and on solids. Much of it is not of an advanced character, indeed is a concise digest of the treatment in larger treatises, but it is very clear, straightforward, non-mathematical, and up-to-date. References are not numerous but are very well chosen, and if followed up will enable the reader to find all important original literature quickly. The sections dealing with spreading on mercury, a subject to which the author has made very important original contributions, are full, and give information not easily found elsewhere; the remainder of the book should serve as an admirable introduction to the whole field indicated in the title.

The price appears somewhat high for a book of this size and class, in paper covers, but its quality is high, and it can be heartily recommended.

N. K. A.

Textile Testing. PHYSICAL, CHEMICAL, AND MICROSCOPICAL. By JOHN H. SKINKLE. (London: Macmillan & Co. Ltd., 1940. Price 15s.) Pp. 269. Tables 27. Illustrations 63.

This book has international significance in that it places before the textile world a complete correlation between testing in its various aspects. In textiles to-day, although science has made such vast strides, yet there is no agreement on methods or interpretation of results, nor could there be such until a lead was taken to collect a representative set of tests together, such as is found here, as a basis for discussion. The book deals with tests of fibre, yarn and fabric, but does not deal so completely with control of actual processing.

If for no other reason, the book is valuable because of its excellent bibliography, which includes so many British references. It is a pity, however, that the author has not included more of the German and Continental work, since it leaves an incompleteness in its international significance. Nevertheless, it is a book that every student should study as a contemporary of his technical textbooks, and every executive and operative should have at hand for ready consultation. The tables should not be taken as wholly authentic in certain cases, since, of necessity, some values have been revised. Nevertheless, they are of the correct order as published and useful for ordinary reference. The book is remarkably concise, and contains no extraneous matter or padding; in fact, it is an excellent example of clear exposition of the many varied aspects of the subject.

S. G. B.



THE PHOTOLYSIS OF MERCAPTANS.

BY N. P. SKERRETT AND N. W. THOMPSON.

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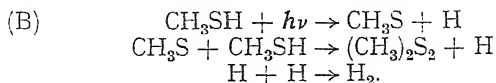
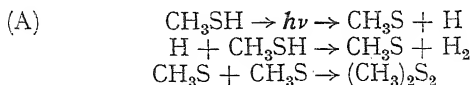
Some observations on the photolysis of alkyl mercaptan vapours were recently summarised.¹ These earlier experiments chiefly concerned ethyl mercaptan; more detailed measurements have now been made with the methyl derivative.

The ultraviolet absorption spectrum of methyl mercaptan is a continuum extending towards shorter wavelengths from 2750 Å., the extinction coefficient increasing rapidly towards higher frequencies. When the vapour is irradiated with the mercury line 2537 Å., a decrease in pressure is observed, which, using initial pressures between 200-600 mm., amounts to about 30 % of the initial value. After completion of the photolysis the gaseous products were withdrawn, washed with concentrated alkali to remove residual mercaptan, and then analysed for hydrogen and hydrocarbons in the standard manner. They appeared to consist of about 80 % hydrogen, 18 % methane, with traces of ethane and a small variable unidentified residue. In addition, during the photolysis a yellow solid and oily yellow liquid are formed. The solid has the properties of sulphur; the liquid is soluble in alcohol or ether, insoluble in water, reacts with nitric acid or dilute bromine water, and appears to be methyl disulphide $(\text{CH}_3)_2\text{S}_2$.

The analytical data suggest that the overall reaction consists mainly of the process $2\text{CH}_3\text{SH} + h\nu = (\text{CH}_3)_2\text{S}_2 + \text{H}_2$, with the concurrent but much less important reaction $\text{CH}_3\text{SH} = \text{CH}_4 + \text{S}$. Secondary photolysis of the methyl disulphide may lead to the small amounts of both sulphur and ethane found. These results are paralleled by those found with ethyl mercaptan, where the main reaction leads to ethyl disulphide and hydrogen and not to ethane. The absorption spectrum of both molecules is closely similar to that of hydrogen sulphide, and unlike those of the alkyl thio-ethers, which absorb electronically only at much shorter wavelengths. For this reason it was inferred previously that the continuum is associated with a primary one-act dissociation involving rupture of the S—H link, giving a hydrogen atom and the RS radical. The subsequent processes will depend on the ability of these primary products to propagate chains. Some information about this may be found from measurements of the quantum yield. A method of measuring the rate of disappearance of methyl mercaptan was therefore devised, based upon its reaction with iodine. This method proved more satisfactory with methyl mercaptan than with the ethyl derivative, and in combination with a uranyl oxalate actinometer appeared to give reproducible values of the quantum yield of about 1.7 molecules of mercaptan decomposing per quantum absorbed.

¹ *Trans. Faraday Soc.*, 1938, **34**, 1238.

Either of the two following schemes of processes would lead to a quantum yield of two :



In either case, the presence of the concurrent primary process $\text{CH}_3\text{SH} \rightarrow \text{CH}_3 + \text{S}$ would reduce this value. A combination of schemes (A) and (B), that is, the ability of both H atoms and CH_3S radicals to react easily with methyl mercaptan molecules, would lead to chain propagation and a higher quantum yield than is found. Of (A) and (B) the former seems more probable both by virtue of the high reactivity of hydrogen atoms, and the ease of recombination of two CH_3S radicals as against that of a pair of hydrogen atoms. It follows, therefore, that the reaction of CH_3S radicals with methyl mercaptan molecules has an appreciable inertia, and the CH_3S radicals a relatively long life.

The earlier measurements with ethyl mercaptan gave a rather higher quantum yield, suggesting chain propagation. There is no reason in principle why the $\text{C}_2\text{H}_5\text{S}$ radical should not be more reactive than the CH_3S radical, but as previously explained, the experimental difficulties with ethyl mercaptan are such that not too much reliance should be placed on values of the quantum yield in this case.

It may be concluded that the lower alkyl mercaptans are photolysed predominantly by the primary process $\text{R-SH} \rightarrow \text{RS} + \text{H}$ and not by the process $\text{RSH} \rightarrow \text{RH} + \text{S}$, which might have been expected on the basis of similar measurements with aldehydes.

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A THERMODYNAMIC STUDY OF BIVALENT METAL HALIDES IN AQUEOUS SOLUTION. PART VII. THE ACTIVITY COEFFICIENT OF BARIUM BROMIDE AT 25°.

By R. A. ROBINSON.¹

Received 4th December, 1940.

The activity coefficients of the three magnesium halides² bear a close resemblance to those of the corresponding lithium and sodium halides. The curves resulting when γ is plotted against \sqrt{m} exhibit a minimum at comparatively low concentrations, 0.2, 0.25, and 0.3 m. for the iodide, bromide and chloride respectively, the activity coefficients reaching values considerably greater than unity at high concentrations. This resemblance to the alkali halides is also found in the chlorides of calcium,

¹ Sterling Fellow, Yale University, 1940.

² Robinson and Stokes, *Trans Faraday Soc.*, 1940, **36**, 733.

strontium and barium,³ the activity coefficient at any given concentration decreasing with increasing atomic number of the cation, the curve for barium chloride being characterised by a very shallow minimum and the activity coefficient rising to only 0.450 at 1.8 M. It has been shown⁴ that the order of the activity coefficient curves, $I > Br > Cl$, which holds for the lithium, sodium and potassium salts is reversed in the case of the rubidium and caesium halides. As a parallelism in many respects can be found between the activity coefficients of the alkali metal and alkaline earth metal halides, the question of some importance arises as to whether a similar reversal in order is to be found for barium halides. To answer this question, isopiestic measurements have been made on barium bromide.

The salt was recrystallised three times from water and used in the form of stock solutions which were analysed for bromide. In Table I are recorded the molalities of isopiestic solutions of $BaBr_2$ and KCl .

TABLE I.—MOLALITIES OF ISOPIESTIC SOLUTIONS OF BARIUM BROMIDE AND POTASSIUM CHLORIDE.

The first of each pair of figures refers to potassium chloride, the second to barium bromide.

0.1253, 0.09092 ;	0.2178, 0.1557 ;	0.4035, 0.2800 ;	0.4355, 0.3012 ;
0.5932, 0.4008 ;	0.7140, 0.4900 ;	0.8110, 0.5303 ;	0.9640, 0.6212 ;
1.126, 0.7098 ;	1.447, 0.8847 ;	1.553, 0.9342 ;	1.772, 1.047 ;
2.429, 1.356 ;	2.552, 1.414 ;	2.586, 1.430 ;	2.772, 1.507 ;
3.117, 1.660 ;	3.375, 1.769 ;	4.165, 2.093 ;	4.736, 2.321 ;

Table II contains the osmotic and activity coefficients of $BaBr_2$ relative to the activity coefficient of KCl given in a previous communication.⁵

TABLE II.—OSMOTIC AND ACTIVITY COEFFICIENTS OF BARIUM BROMIDE AT 25°.

m.	ϕ .	γ .
0.1	0.848	(0.513)
0.2	0.850	0.465
0.3	0.854	0.446
0.4	0.869	0.438
0.5	0.887	0.437
0.6	0.907	0.439
0.7	0.928	0.444
0.8	0.948	0.452
0.9	0.970	0.463
1.0	0.994	0.473
1.2	1.019	0.500
1.4	1.066	0.534
1.6	1.168	0.572
1.8	1.229	0.616
2.0	1.271	0.666
2.2	1.319	0.719
2.4	1.369	0.776

The value of $\gamma = 0.513$ at 0.1 M. has been adopted provisionally, since at low concentrations the osmotic coefficients of $SrCl_2$ and $BaBr_2$ approximate to one another closely.

Gelbach and Huppke⁶ made e.m.f. measurements which also gave the activity coefficient of barium bromide. Their reference value of $\gamma = 0.716$ at 0.01 M., obtained by comparison with $BaCl_2$, should be revised to 0.740 on the basis of more recent work. On this basis the comparison in Table III may be made; this table also contains the results from freezing-

TABLE III.

m.	0.1.	0.2.	0.3.	0.5.	1.0.
(F.Pt.)	0.513	0.468	—	0.439	0.465
(Gelbach)	0.511	—	0.442	0.442	0.431
(Robinson)	0.513	0.465	0.446	0.437	0.473

³ Robinson, *Trans. Faraday Soc.*, 1940, **36**, 735.

⁴ Robinson, *J. Amer. Chem. Soc.*, 1935, **57**, 1101; 1937, **59**, 84.

⁵ Robinson, *Trans. Faraday Soc.*, 1939, **35**, 1217.

⁶ Gelbach and Huppke, *J. Amer. Chem. Soc.*, 1926, **48**, 1504.

point measurements computed by Redlich and Rosenfeld,⁷ not corrected for the temperature difference.

Although the agreement between the three sets of results is only moderate, there is no doubt but that the activity coefficient of barium bromide is higher than that of barium chloride and there is no reversal of order as in the case of the rubidium and caesium halides. The dispersion between the curves of the chloride and bromide is not only in the opposite direction, but is much greater than was found for the alkali metal salts.

Summary.

An isopiestic determination of the activity coefficient of BaBr_2 at 25° has shown that BaBr_2 gives an activity coefficient curve considerably higher than that of BaCl_2 , and that no reversal in order of the chloride and bromide occurs. In this respect the barium salts are unlike the rubidium and caesium salts.

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⁷ Landolt-Börnstein, "Tabellen," 2er, Erg. p. 1114.

CRYSTALLISATION PHENOMENA IN RAW RUBBER.

By L. R. G. TRELOAR.

Received 21st December, 1940.

In an earlier paper¹ the author has shown that the plastic flow in raw rubber does not, in general, increase continuously with increasing extension, but after rising to a maximum at an intermediate extension, falls again as the extension is further increased. In the region of extension corresponding to the position of this maximum there is a change in the nature of the recovery phenomena. Below the maximum the recovery is gradual, and increases with each successive increase of temperature, whilst beyond it almost complete retraction takes place within a very narrow range of temperature. These and other associated phenomena were interpreted as manifestations of a change from the amorphous to the crystalline state of rubber, a change which has already been demonstrated by X-ray diffraction experiments.²

The aim of the present experiments was to determine more precisely the relative amounts of the crystalline phase present in raw rubber under various conditions of extension. For this purpose measurements of double refraction were carried out at various temperatures under conditions of extension similar to those used in the mechanical tests previously described,¹ and the changes in density which accompany the extension at a particular temperature (0°C.) were investigated. Taken together these methods have enabled a reasonably complete picture of the development of crystallisation under various conditions of extension and temperature to be obtained.

¹ Treloar, *Trans. Faraday Soc.*, 1940, **31**, 538.

² Katz, *Chem.-Ztg.*, 1925, **49**, 353.

The Measurement of Birefringence.

When stretched, a strip of rubber acquires the optical properties of a uniaxial crystal, the direction of the extension corresponding to the optic axis. Monochromatic light polarised in a plane making an angle of 45° with the optic axis is decomposed on passing normally through the strip into two components polarised in planes respectively parallel and perpendicular to the axis, and differing in phase by an amount δ . The birefringence may conveniently be represented as the optical path difference in wavelengths of light per mm. of thickness of the rubber. Denoting this quantity by B , the thickness of the rubber by t and the wavelength of the light in vacuo in mm. by λ , the difference of the two principal refractive indices of the material is given by the relation

$$n_1 - n_2 = B\lambda = \lambda\delta/2\pi t.$$

The rubber films used in the optical experiments were prepared from a viscous solution of crepe in benzene by evaporation from a free drop floating on a mercury surface. By controlling the rate of drying the resultant films were obtained perfectly flat and of uniform thickness, and, so far as could be judged, entirely free from internal strain. The dried films (thickness 0.1 to 0.2 mm.), after removal from the mercury, were washed with sodium stearate solution. This was found to prevent self-adhesion during handling, without reducing the optical transparency.

The specimens used had a length of 20 mm. between clamps and a width of 5 mm. Light polarised at an angle of 45° to the direction of stretch passed normally through the specimen, which was observed through a low-power microscope provided with a Babinet compensator and analysing Nicol prism.*

With instantaneous stretching it was not possible to use monochromatic light, because the passage of the interference fringes across the eyepiece during the extension could not be followed. White light was therefore used. This involved some difficulty owing to the dependence of the birefringence on wavelength, which caused a spurious shift of the central black band. This effect was studied in a preliminary experiment in which the stretching was carried out slowly, the displacement of the central fringe when sodium light was used being compared with the displacement of the fringe system in white light. Both vulcanised and raw rubber were examined and found to give the same characteristic effects. With white light the central black band became spread out into a spectrum as its displacement increased, and the first order coloured fringes began to merge together. When the shift in sodium light amounted to 6 fringes the dark band in white light had apparently been displaced by an amount equivalent to 7 fringes. With further extension this series of changes began to repeat itself.

With this preliminary experience it was possible, in the instantaneous stretching experiments, to assign the true displacement (which was not more than 9 fringes) corresponding to the observed displacement of the central band. In calculating the optical path difference per mm. for a particular extension the strained thickness of the rubber was assumed to be $t_0(l_0/l)^{\frac{1}{2}}$, where l_0 and l are the original and extended lengths respectively, and t_0 the original thickness; t_0 was obtained by weighing, using the measured value of density for the rubber.

* We have to thank Messrs. James Swift & Son, of 81 Tottenham Court Road, London, for the construction of the optical apparatus to our special requirements.

The Birefringence at 0° C.

In carrying out the experiments at 0° C.† the specimen, mounted on a metal frame, was supported in a glass tube closed at its lower end and immersed in a water-ice mixture contained in a cylindrical Dewar vessel which acted as a thermostat. The Dewar vessel was provided with two unsilvered strips along its length to permit the passage of light and observation of the specimen. Each specimen was stretched instantaneously by means of a falling weight, after which the movable clamp was fixed in position, and the stretching apparatus removed. The temperature of the bath was maintained at 0° C. by removing the apparatus to the refrigerator between readings.

The experimental data thus obtained are given in Fig. 1. At high elongations the birefringence is seen to reach a high value immediately after stretching and thereafter to change only slightly, but at the lower

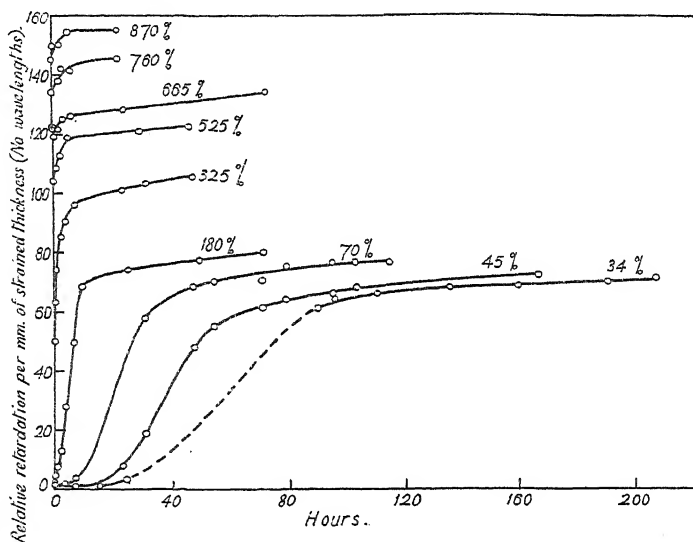


FIG. 1.—Time changes in birefringence in crepe held at the extensions indicated at 0° C.

elongations the approach to the saturation value is very much slower. Evidently the rate of crystallisation varies enormously with the extension, the final state being approached in a fraction of a second at the highest extension, but requiring 100 hours or more at the lowest extension employed.

Appearance of Fringes.—During the observations marked variations in the intensity and uniformity of the interference fringes were noticed. At the higher extensions the fringes were uniform and clear. At an intermediate extension (325 %), the fringes were weak and irregular in the early stages, but gradually became clearer and more uniform as the crystallisation progressed. At low extensions the phenomena were again different. Thus, at 70 % extension the fringes were clear and regular at first (*i.e.* before appreciable crystallisation had occurred) but became very faint and irregular after 7 hours. After 50 hours they increased in intensity, but continued to be rather irregular for the rest of the time. At 34 % extension

† Care was taken to remove any crystallisation in the film which might have occurred spontaneously at room temperature.

the fringes were clear at first but became fainter as crystallisation progressed. After 25 hours they had become invisible, and readings could not be taken until 90 hours from the start, when they reappeared, becoming fairly clear by the end of the experiment. An attempt was made to work at 20 % extension, but the fringes finally disappeared after 80 hours, and did not reappear.

To account for these changes, two effects have to be considered. They are (1) patchy crystallisation, causing irregularities in the fringes, particularly in the region of incomplete crystallisation, and (2) disorientation of crystal axes discussed later), leading to scattering of light at the lower extensions.

The Birefringence-Elongation Relationship.—When the saturation values of birefringence are plotted against elongation (Fig. 2, curve *c*), the points are seen to fall nearly on a straight line. This line, however, does not pass through the origin. This fact is rather surprising, because in unstretched rubber the crystals have no preferred orientation. The birefringence must therefore become zero at zero elongation, *i.e.* the birefringence-elongation curve must pass through the origin.

In attempting to understand how this apparent discrepancy arises, the assumption will be made that the birefringence at any elongation is determined by two factors, (1) the total amount of crystalline material, and (2) the orientation of the crystallites. Now it is known from the work of Bekkedahl³ that rubber increases in density by about 2.65 % when crystallised by freezing in the unextended state. It is therefore possible, by studying density changes, to estimate the amount of crystallisation directly, and thus to eliminate the effect of orientation. Experiments on these lines will now be considered.

Density Changes at 0° C.

Preliminary experiments were carried out with smooth-rolled smoked sheet. This was subsequently not used because it was found by visual observations that neighbouring portions of the sheet crystallised at widely different rates. The reason for these differences was not investigated, but the experiments revealed the importance of working with a material which was originally homogeneous. Further work was therefore carried out with a 2-mm. sheet of crepe prepared by evaporation of a solution. For this purpose a 7 % solution of rubber in benzene + 4 % alcohol was poured on to the surface of mercury, using a paper edging to allow of free contraction during drying. The sheet thus prepared was of uniform thickness and free from air bubbles. The crepe was taken from the same batch of rubber as that used in the optical experiments.

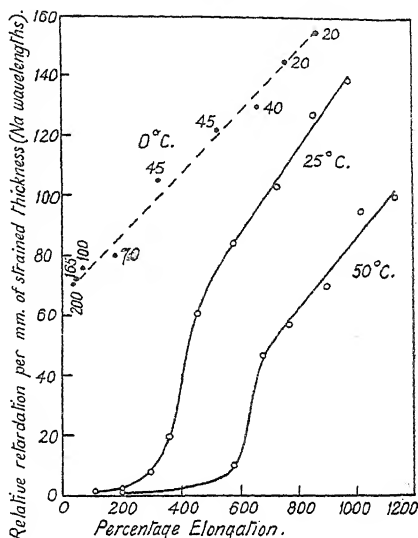


FIG. 2.—Relation between birefringence and elongation for crepe.
25° and 50° after 1 hour
0° after hours indicated

³ Bekkedahl, *Nat. Bur. Stds. J. Res.*, 1934, 13, 411.

For the zero-extension experiment, a piece of the sheet was hung in a tube in a Dewar vessel containing ice-cold water. The specimen was quickly transferred to a beaker of water at 0°C . when it was required to measure the density, after which it was replaced. Readings were taken over a period of 3 weeks. For the experiments involving the application of an extension, parallel marked strips cut from the sheet were gripped between clamps in a bath of ice-cold water. The stretching was carried out by quickly pulling by hand on a wire attached to the movable clamp, after which the stretched strip (still at 0°C .) was firmly clamped down to a stout board at each end, and at three other points along its length. This arrangement enabled four separate specimens to be subsequently removed at intervals for density measurements. The rubber strip mounted on the board was kept in the intervals between measurements in a lagged box in the refrigerator. The temperature registered on a thermometer placed alongside the rubber varied between 0° and -3°C . during the course of the experiments; the temperature control was thus not so good as in the optical experiments.

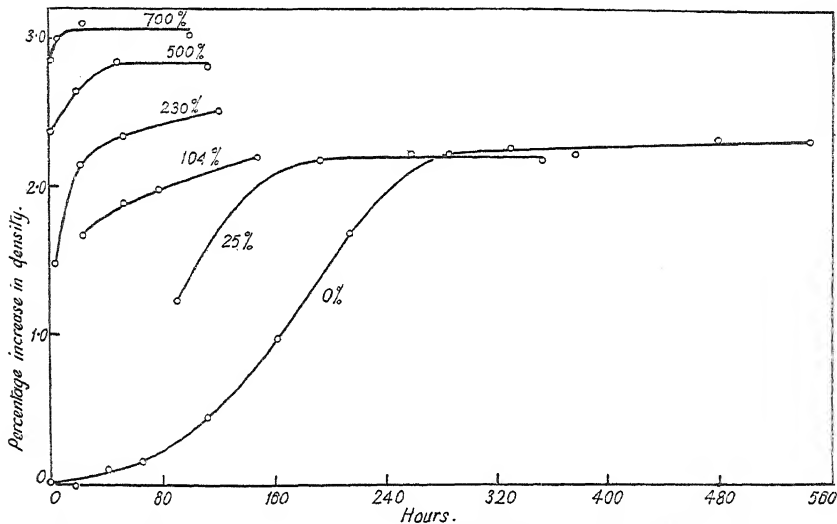


FIG. 3.—Time changes in density in crepe held at the extensions indicated at 0°C .

The density was measured by weighing the rubber in air and in water at 0°C ., the rubber being supported in a light frame of copper wire hung from the arm of the balance. Actually the temperature of measurement differed from 0°C . by a fraction of a degree, and the data were corrected for the variation in density of the water and of the rubber on this account. For this purpose the coefficient of expansion of the rubber was taken as $67 \cdot 10^{-5}$ per degree.⁴ The accuracy of the determination was limited chiefly by the quantity of rubber used. This varied from 0.27 g. at the highest to 1.0 g. at the lowest extension. At the highest extension the errors of measurement were believed to be within 0.1%. The results of these measurements are given in Fig. 3, which shows the variation of density with time for a number of extensions.

Interpretation of Birefringence and Density Data.

The general similarity between the curves representing the changes in birefringence at various elongations, and those representing the changes in

⁴ Wood, *Rubber Chem. Tech.*, 1939, 12, 130.

density is at once apparent. Both the rate of increase of density and its saturation value show a marked dependence on elongation. If the birefringence, like the density, depended solely on the total amount of crystalline material, then the ratio of the birefringence B to the change of density $\Delta\rho$ would remain constant as the elongation varied. Any departures from constancy of this ratio may be taken as indicative of the effect of the orientation factor on birefringence. The values of the ratio $B/\Delta\rho$ for five different extensions are set out in the accompanying table. For the first four extensions the values of B were obtained by interpolation between the experimental curves of Fig. 1, whilst for the lowest extension the values of $\Delta\rho$ (Fig. 3) were interpolated. The figures for the final states of crystallisation, which are of chief interest, are set out in a separate column, in which also the data for the highest extension have been corrected to take account of the contraction of length (amounting to about 4 %) which occurred on cutting this specimen from the board. The optical experiments showed that for an extension of 700 % this contraction on releasing the tension was accompanied by a reduction of birefringence by 5.6 %. This amount was therefore subtracted from B so that the figures for B and for $\Delta\rho$ should both relate to the same state of the rubber. For the remaining extensions there was either a negligibly small contraction or a slight increase in length, so no correction was necessary.

In considering the figures in the last column of Table I, it is necessary to bear in mind the rather large experimental errors involved. It is difficult to estimate these exactly, but it is thought that the probable error in $B/\Delta\rho$ may be as much as ± 5 %.

From 10.4 % to 700 % elongation the final variations in $B/\Delta\rho$ are seen to be only slightly outside the limits of experimental error, though there is an indication of a slight increase in this quantity with increasing extension. Only at the lowest extension (34 %) was a definitely different value of $B/\Delta\rho$ obtained, but even here it was only 20 % lower than at the highest extension employed. The $B/\Delta\rho$ values corresponding to the shorter times, when crystallisation was still not completed, show a greater variation. Part of this variation is probably due to slight differences in the conditions in the two sets of experiments (*e.g.* in rate of extension, degree of temperature control) which may have affected the respective rates of crystallisation.*

The fact that the saturation values of birefringence are approximately proportional to the changes in density at all but the lowest extension is of considerable importance. It shows that the birefringence gives a quantitative measure of the amount of crystallisation over a very wide range of

TABLE I.—VARIATIONS IN THE RATIO OF BIREFRINGENCE TO CHANGE OF DENSITY UNDER DIFFERENT CONDITIONS OF EXTENSION.

Elongation %.	Time (Hours).	$B/\Delta\rho$.	$B/\Delta\rho$ (Final).
700	1.3	44.5	—
700	6	44.0	—
700	22	43.9	41.4*
500	1.2	43.0	—
500	20	44.5	—
500	72	43.4	43.4
230	3.5	33.1	—
230	22	38.6	—
230	72	37.6	37.6
10.4	24	31.7	—
10.4	52	38.4	—
10.4	115	37.6	37.6
34	89	46.3	—
34	207	32.3	32.3

* Corrected.

* The temperature rise during stretching (Joule effect) will almost certainly be different in the two cases.

elongations. It shows further that a very considerable degree of orientation of the crystallites has already been achieved with an extension of only 34 %, and that beyond that extension the increase in birefringence is due almost entirely to an increase in the amount of crystalline material present, which continues at a fairly uniform rate right up to the breaking-point.

The precise meaning to be attached to the phrase "very considerable degree of orientation" requires a detailed examination of the relation between the degree of orientation and the resulting birefringence. Such a theoretical investigation is described in an appendix to this paper. From this it appears that the birefringence is not very sensitive to departures from the state of perfect orientation.

Experiments at 25° and 50° C.

The optical data obtained at higher temperatures will now be considered. Fig. 4 shows the variations in birefringence over a period of

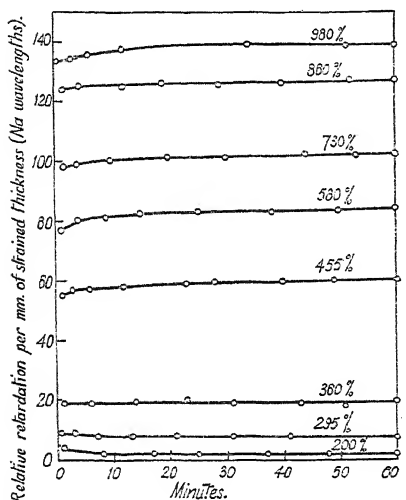


FIG. 4.—Time changes in birefringence in crepe held at the extensions indicated at 25° C.

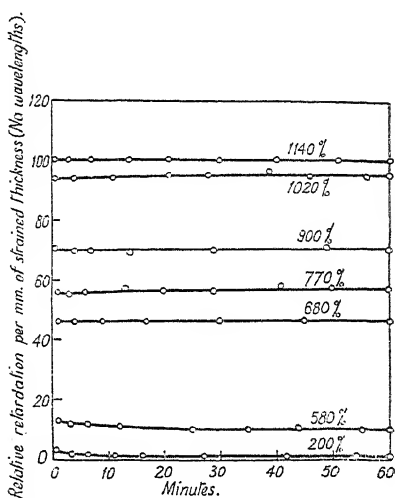


FIG. 5.—Time changes in birefringence in crepe held at the extensions indicated at 50° C.

1 hour in specimens of crepe stretched to various elongations at 25° C. The following features of these curves should be noted:—

1. Below 360 % extension the birefringence tends to fall, the rate of fall becoming less with the lapse of time.
2. From 360 % onwards the birefringence either remains constant or shows a slight increase, this increase being most marked in the early stages.

Corresponding data for a stretching temperature of 50° C. are shown in Fig. 5. At this temperature the transition from the falling to the rising type of curve occurs at a higher extension, namely 680 %. Whilst the falling tendency at the lower extensions is more marked at this temperature, the rise at the higher extensions is less conspicuous.

If the birefringence at the end of the 1-hour period is plotted against the elongation (Fig. 2, curves *a* and *b*), it is seen that at an elongation corresponding to the transition from the falling to the rising birefringence curve there is a rapid increase in the magnitude of the birefringence. Following this rather sudden jump there is a further steady increase as the elongation is increased up to the breaking-point.

Interpretation of Experimental Results.—The X-ray work of Gehman and Field⁵ and others shows that the crystals formed when raw rubber is stretched at room temperature or higher lie with their axes very nearly parallel to the stretching direction, even when the amount of crystalline material present is only just sufficient to produce a diffraction pattern. It may therefore be concluded that the birefringence provides a quantitative measure of crystallisation except at the low extensions, before the sudden rise. At these low extensions the optical activity may be due either to incipient crystallisation or to a partial alignment of molecules, without crystallisation, or both. The curves show a close resemblance to the data for vulcanised rubber given by Thiessen and Wittstadt,⁶ except that the fall in birefringence corresponding to the lower extensions, which is presumably connected with the release of internal strain, was not present in their case.

From the curves for the higher elongations in Figs. 4 and 5 it is seen that the final state of crystallisation is not attained instantaneously, though it is approached more quickly at 50° than at 25° C. This may be accounted for by the greater mobility of the molecules at the higher temperature. A similar time-lag in the development of crystallisation in vulcanised rubber was observed by Thiessen and Wittstadt,⁶ using optical methods, and had been demonstrated earlier by Long, Singer and Davey⁷ by X-ray methods.

Appearance of Fringes.—As at 0° C. the transition from the amorphous to the crystalline state was accompanied by certain characteristic changes in the interference fringes. Whilst at low elongations they were clear and parallel, at intermediate elongations they became less intense and very irregular, indicating that crystallisation had not proceeded to the same degree at all points of the rubber. A number of peaks in the fringes could be distinguished running along the length of the specimen, suggesting a sort of fibrous crystallisation. At higher extensions the fringes became clearer and more regular, though they did not regain entirely their original regularity. The greatest irregularity was observed at extensions of 360 % and 455 % in the 25° experiments, and at extensions of 580 % and 680 % in the 50° experiments. These were the regions where the degree of crystallisation was changing most rapidly with elongation. These observations indicate that in the early stages the crystallisation is not uniform throughout the rubber, there being comparatively large crystalline patches interspersed with amorphous "spaces." As the extension is increased these "spaces" fill up with crystalline rubber, thus producing a more uniform texture.

Check on $B/\Delta\rho$.—Since at these temperatures the orientation of the crystallites is high, even when the amount of crystallisation is small, the change of density accompanying the extension should be proportional to the birefringence, the constant of proportionality having the value found at the higher extensions at 0° C. To check this point an additional experiment was carried out in which both the birefringence and the density change were measured on the same specimen of rubber. A strip of crepe film 5 cms. wide and 0.7 mm. thick was extended to 700 % elongation and left for 20 hours at room temperature (about 20° C.). A piece was then cut off and examined optically. Since the fringe shift was well beyond the range of the compensator, a number of calibrated cellophane sheets were interposed to bring the dark band into the field of view. The resultant shift, after correction for the spurious displacement of the central band, was 29.4 sodium fringes, the corresponding value of B being 106.5 fringes per mm. The uniformity of the crystallisation was shown by the fact that even with this large displacement the fringes were easily visible,

⁵ Gehman and Field, *J. Appl. Physics*, 1939, 10, 564.

⁶ Thiessen and Widdstadt, *Z. physik. Chem. B*, 1938, 41, 33.

⁷ Long, Singer and Davey, *Ind. Eng. Chem.*, 1934, 26, 543.

and their displacement was uniform over the whole specimen. The density change, measured on the same specimen at the same temperature, 20° C., was 2.57 %, giving $B/\Delta\rho = 41.4$. This agrees well with the high-extension values in Table I.

Correlation with Mechanical Properties.—The facts brought out in these optical experiments confirm the conclusions arrived at by the author from the study of the plastic flow and recovery phenomena.¹ If, as is believed, the development of crystallisation takes place through a grouping together of neighbouring portions of long-chain molecules, the effect of the crystallisation will be to increase the cohesion between molecules in certain regions, and thus to increase the effective viscosity of the bulk material. It is therefore to be expected that the plastic flow will begin to fall at that extension at which crystallisation sets in. Using the plastic flow data given in the earlier paper, the agreement is found to be reasonably close, as the following table shows:—

TABLE II.—COMPARISON OF OPTICALLY DETERMINED CRYSTALLISATION POINT WITH MAXIMUM IN PLASTIC FLOW/ELONGATION CURVE.

	Temperature.	
	25°.	50°.
Optical crystallisation point at elongation of	300 %	550 %
Maximum plastic flow at elongation of	300 %	450 %

The birefringence also shows a close correlation with the development of a sharply-defined retraction temperature, a phenomenon directly related to the state of crystallisation. It is interesting to note that the existence of such a definite retraction temperature does not imply *total* crystallisation; in fact, the present data, taken in conjunction with the earlier work, show that it may occur when the crystallisation has reached no more than 50 % of its maximum value.

With the optical, as with the mechanical properties of raw rubber, the rate of extension is of great significance. The above findings hold good only when the elongation is carried out very quickly. This may be illustrated by an experiment in which crepe rubber was extended slowly at 25° C. over a period of 30 minutes. In this case crystallisation first appeared at an elongation of 600 %, compared with 300 % in the quick-stretching experiments.

Discussion.

X-ray analysis would appear to offer the best hope of finding a solution to some of the problems raised by the present investigation, particularly the questions of the angular distribution of the crystallites and the relative amounts of crystalline and amorphous rubber present under different conditions of extension. Some interesting work along these lines has already been carried out by Gehman and Field,⁵ who extended rubber at room temperature and subsequently froze it at -5° C. for 18 hours. They were able to demonstrate a gradual transition from the Debye-Scherrer ring pattern, obtained with unstretched rubber, to the fibre pattern as the extension was increased up to about 350 per cent. Definite evidence of orientation was observed with an elongation of only 30 per cent. Although obtained under rather different experimental conditions, these data give some support to the conclusions drawn from the present optical experiments.

A view of the underlying process of crystallisation which seems to account in a satisfactory manner for many of the observed phenomena has been put forward by Gehman and Field. Starting from Tammann's conception of crystallisation in a supercooled liquid, they consider that there are in rubber variations in the local state of order of adjacent molecules or parts of molecules, the most highly ordered regions acting as incipient nuclei for crystal growth. The probability of the formation of such ordered regions would naturally be increased either by mechanical extension or by a reduction of temperature. Thus at low temperatures "centres, which may consist merely of an approximate parallelism of neighbouring portions of long-chain molecules, become effective for crystal growth."

The idea of the growth of crystals round nuclei accounts for the characteristic S-shape of the birefringence and density curves for rubber extended to low elongations at 0° C. (Figs. 1 and 3). For if the rate of crystallisation is determined by the total surface area of the nuclei at each instant of time, it will obviously increase continuously as the crystallisation progresses, until the point is reached where the regions of potential growth of the individual crystallites begin to interfere with each other. Beyond this point the rate of crystallisation will become progressively slower with advancing time.

In contrast to the behaviour of an ordinary low-molecular liquid, the crystallisation process in a rubber would not be expected to continue to completion. The reason for this difference is to be found not only in the more or less permanent linkages between the long-chain molecules of the rubber, which it is necessary to postulate in order to account for its observed elastic properties, and which will interfere with the proper development of the crystal lattice, but also from the mere fact that the rubber molecule is a long randomly-kinked chain. On account of this last fact it is to be expected that portions of the same molecule may be found in two or more separate crystalline regions. Owing to the restrictions to their movement imposed by their attachment to the crystals, the intervening portions of such molecules will be very difficult to fit into a crystalline lattice. This difficulty will increase rapidly as the amount of crystalline material formed increases, until a point is ultimately reached when further crystallisation is no longer possible, even though an important portion of the rubber may still be in the amorphous state.

At low temperatures the application of an extension will not only increase the number of crystal nuclei present, but will also affect their orientation. We have seen that even at quite low extensions this orientating effect is considerable. In fact, to account for the optical data it is necessary to assume that the degree of orientation of the nuclei is very much higher than that of the rubber molecules as a whole. This can be proved indirectly by another observation, namely that the process of crystallisation is accompanied by an increase of length of the stretched specimens. This "secondary elongation," according to Park,⁸ reaches a maximum of about 4 per cent. of the stretched length in the region of 200 % to 300 % elongation. If the crystal nuclei had the same angular distribution as the molecules as a whole, there would be no reason for a change of shape during crystallisation, but if the nuclei are more highly orientated than the molecules as a whole, then,

⁸ Park, *Memoirs College Sci. Kyoto Imp. Univ.*, 1939, **22**, 13.

as pointed out by Smith and Saylor,⁹ an increase of length during crystallisation is to be expected.

Another result of the extension is to increase the total amount of material finally brought into the crystalline state. It is suggested that this is due simply to the increased alignment of the molecules, which are now more readily fitted into a lattice owing to the reduction in the number and complexity of the portions of molecules which happen to be in the wrong directions with respect to their neighbours. How closely the state of the rubber at the breaking-point approximates to 100 % crystallisation cannot be determined from the present experiments, but it is clear that there will always be an appreciable proportion of the molecular chains not fitted into a lattice, however great the extension.

From the picture of the semi-crystalline state of rubber thus arrived at, it is not difficult to understand why a comparatively small amount of crystallisation exerts such a profound effect on the plastic flow. It is seen that on account of the molecular ties between the crystals and the amorphous rubber, or directly between crystals, the freedom of movement of the crystals one over another will be greatly impeded. Mechanically, the crystallisation may be regarded as introducing a large number of new cohesional linkages between the molecules. It is the number and strength of these cohesional linkages which determines the bulk viscosity of the material. If this picture is the correct one, it follows that the transition from a given partially extended crystalline state to a state of higher (or lower) extension cannot be brought about simply by rotation of the crystals already formed. Some degree of breakdown of the original crystal pattern will necessarily be required in order that the molecules may move into the new positions which the extension forces them to take up. This effect may be observed through its influence on the birefringence. In a particular experiment a piece of rubber which had been extended to 260 % elongation and allowed sufficient time at 0° C. for the completion of crystallisation was subjected to a further deformation at this temperature, whereby its elongation was increased to 470 % (compared with the unstretched length). In spite of the increased elongation the birefringence immediately fell, and it was only after the lapse of time that it eventually rose to a value higher than that which it possessed at the original elongation.

Minimum Density of the Rubber Crystal.—It has already been stated that the present experiments do not provide any means of determining the absolute, as distinct from the relative amounts of crystallisation in rubber. It is therefore not possible to determine the density of the rubber crystal, because even under the most favourable conditions there remains an unknown proportion of uncrystallised material. It is only possible to assign a lower limit to this density.

The highest state of crystallisation was achieved at 870 % extension at 0° C.—an extension very near the breaking-point. The birefringence in this state was 155.0 sodium wavelengths per mm. Taking 41.4 as the best value of $B/\Delta\rho$ in this region, the corresponding value of $\Delta\rho$ is 3.75 %. The amorphous rubber used in these experiments had a density of .924₅ at 0° C. The minimum density of the rubber crystal at 0° C. is thus .959₂. This figure might be further increased if allowance could be made for the presence of a proportion of non-rubber constituents in the crepe. The density of pure rubber appears to be no different from that

⁹ Smith and Saylor, *Nat. Bur. Stds. J. Res.*, 1938, 21, 257.

of the crude material (Wood),⁴ but the impurities must reduce to some extent the maximum degree of crystallisation achieved. Bekkedahl,³ for instance, has shown that for crystallisation in the unstretched state the change of density is greater with purified rubber than with smoked sheet.

Even without this correction the change of density of 3.75 % calculated from these experiments is higher than any directly measured change previously published. It is interesting to note, however, that Van Rossem and Lotichius¹⁰ observed an increase of density of 3.1 % in rubber which had been "frozen" for several years, a figure noticeably higher than that previously given by Bekkedahl.

Appendix. Effect of Orientation on Birefringence.

In order to examine the effect of the orientation factor on birefringence, a calculation was made of the fringe shift to be expected when polarised light is passed through a number of superposed birefringent crystals variously orientated. For this purpose it was necessary to make an arbitrary choice of the law according to which the crystal axes are distributed in angle; the manner of making this choice obviously will not affect the general nature of the result obtained. The type of distribution chosen is illustrated in Fig. 6. It was obtained simply by projecting a circle containing the appropriate number of equally spaced diameters into an ellipse. The degree of orientation is characterised by the parameter a/b , the ratio of the principal axes of the ellipse.

The calculation was made for a succession of 10 crystals, each introducing a phase difference p between the two components of the light transmitted through it.

The light was then assumed to pass through a quartz wedge, introducing a phase difference q , and finally through the analysing Nicol. The analysis yielded a number of terms representing components of the transmitted light having phase shifts $0, p, 2p, \dots, 10p$, and $q, p + q, \dots, 10p + q$. A graphical combination of these terms then yielded for any value of p the corresponding value of q required to make the resultant intensity a minimum, *i.e.* the compensator setting for a dark band. This will be referred to as the resultant phase shift.

Taking first a uniform distribution of the crystal axes, corresponding to zero extension, the resultant phase shift was calculated for $p = 30^\circ$, using three different random orders of succession. The values obtained were respectively $0^\circ, +4^\circ$ and -5° , the average numerical value being therefore 3° . This is only 1 % of the total phase shift which would occur if all the crystal axes were in the same direction, and confirms that the model chosen contains a sufficiently large number of crystals to yield results of statistical accuracy. With a larger phase shift per crystal, namely 60° , the effect of the particular order of succession chosen was apparent, and with $p = 120^\circ$ the model became unworkable. The results

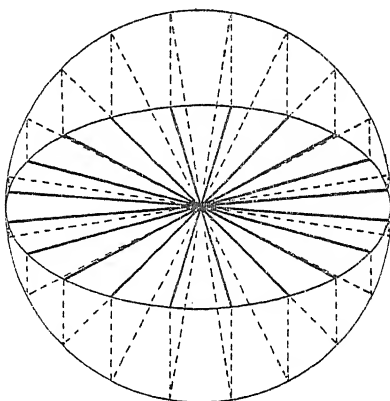


FIG. 6.—Illustrating type of angular distribution assumed.

¹⁰ Van Rossem and Lotichius, *Kautschuk*, 1929, 5, 2.

are therefore applicable only for small values of p , which means in practice that the crystals must be small.

Taking a particular random order of succession, the resultant phase shift was then calculated for different values of a/b , the phase shift per crystal being 30° . The results of these calculations are given in Fig. 7. The curve starts from the origin, and approaches the limiting value of

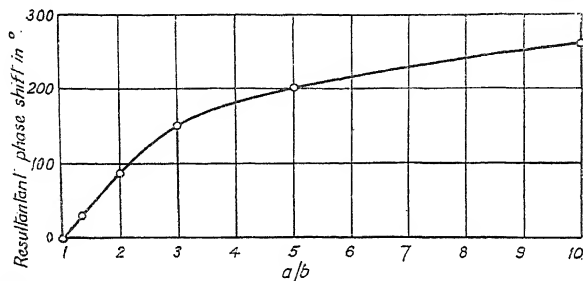


FIG. 7.—Birefringence calculated on 10-crystal model. Phase shift per crystal = 30° .

300° for large values of a/b . This shows that the birefringence is insensitive to small departures from perfect orientation.

It is not possible to relate a/b directly to elongation, but it may be assumed that a plot of the resultant phase shift against elongation, instead of against a/b , would yield a curve of the same general form. To obtain the form of the birefringence-elongation curve when both the orientation and the amount of crystalline material depend on elongation some assumption must be made as to the dependence of the second of these two factors on elongation.

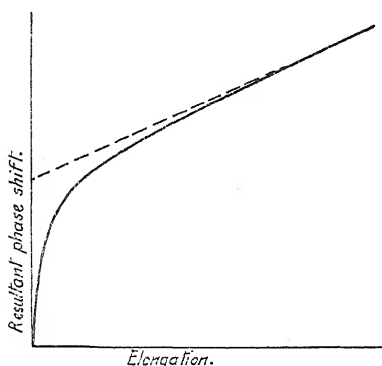


FIG. 8.—Expected birefringence-elongation curve from combined effect of orientation and increase of quantity of crystalline material.

If we assume that the total amount of crystalline material is a linear function of elongation, the birefringence-elongation curve will take the form shown in Fig. 8. This agrees well with the experimental curve over its linear portion but not over its curved portion (*cf.* Fig. 2c). To account for the whole of the experimental data it is necessary to assume that the curved portion occurs wholly below the lowest extension at which observations were made, that is to say, that a considerable orientation has already taken place at this low

extension. The analysis, therefore, leads to the same conclusions as those arrived at from consideration of the density changes.

Summary.

The process of crystallisation in raw rubber held at various extensions at 0° C. has been studied by following the accompanying changes in double refraction and in density. From a comparison of the two sets of data it is concluded that a very low extension produces a relatively high degree of orientation of the axes of the crystallites in the direction of the extension.

From 100 % extension to the breaking-point the increase in birefringence with elongation is due almost entirely to an increase in the amount of crystalline rubber present; over this range the birefringence therefore gives a quantitative measure of the amount of crystallisation.

From the study of birefringence at 25° and 50° C. it appears that crystallisation sets in rather rapidly at a certain intermediate elongation and then increases continuously up to the breaking-point. The observed changes in crystallisation show a close correlation with the plastic flow and elastic recovery phenomena.

The bearing of these observations on the molecular structure of rubber and its mode of crystallisation is discussed. It is estimated that the increase of density of rubber on crystallising is not less than 3.75 %.

The author desires to acknowledge the helpful co-operation of Dr. J. K. Roberts, of the Laboratory of Colloid Science, Cambridge, throughout the course of this work, which forms part of the programme of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

THE ETHANE-ETHYLENE-HYDROGEN EQUILIBRIUM.

BY E. A. GUGGENHEIM.

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1. Introduction.

An analysis of the ethane-ethylene-hydrogen equilibrium and a comparison between the calculated and experimental values of the equilibrium constant were made by Teller and Topley,¹ and simultaneously by Smith and Vaughan.² In both papers it was assumed that in the ethane molecule the twisting mode was effectively a free rotation, although it had been pointed out by Wagner³ that the value found by Heuse⁴ for the heat capacity at 191° K. was inconsistent with this assumption. The more recent accurate measurements of heat capacity at low temperatures by Kistiakowsky and Nazmi,⁵ and by Hunsmann⁶ have established beyond reasonable doubt that the internal twisting mode is far from free. These experimental data, as well as the earlier data at higher temperatures of Heuse⁴ and of Eucken and Parts,⁷ are all consistent with the assumption of a twisting potential energy u of the form

$$u = u_0 \sin^2 \left(\frac{\phi}{3} \right), \quad \dots \quad (1, 1)$$

where ϕ is the angle defining the relative position of the two methyl groups and $u_0/k = 1570$ deg. It is of interest to know to what extent this assumption concerning the twisting mode is in agreement with the experimental data for the ethane-ethylene-hydrogen equilibrium.

¹ Teller and Topley, *J. Chem. Soc.*, 1935, 876.

² Smith and Vaughan, *J. Chem. Physics*, 1935, 3, 341.

³ Wagner, *Z. physikal. Chem. B*, 1931, 14, 166.

⁴ Heuse, *Ann. Physik*, 1919, 59, 86.

⁵ Kistiakowsky and Nazmi, *J. Chem. Physics*, 1938, 6, 18.

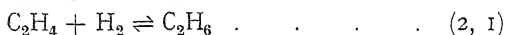
⁶ Hunsmann, *Z. physikal. Chem., B*, 1938, 39, 23.

⁷ Eucken and Parts, *ibid.*, 1933, 20, 184.

Kemp and Pitzer⁸ have compared calculated and experimental values at the single temperature 863° K., and they found satisfactory agreement, but surprisingly no one has to my knowledge published a detailed comparison of theory and experiment over the whole temperature range. Such a comparison seems well worth while, and is given in this paper. The result of the comparison is that throughout the whole temperature range the agreement between theory and experiment is complete. I have endeavoured to set out the results of my calculations in such a form that other authors can check, and possibly improve on, the calculation of any one term in the thermodynamic functions without the necessity of repeating the whole of the lengthy calculations *de novo*.

2. Notations and Formulæ.

The equilibrium constant K_p for the reaction



is defined by
$$K_p = \left[\frac{p_{\text{C}_2\text{H}_6}}{p_{\text{C}_2\text{H}_4} p_{\text{H}_2}} \right]_{\text{equilibrium}} \quad (2, 2)$$

where p denotes a partial pressure. K_p is related to the Gibbs function G , the total heat H , the chemical potentials μ , and the absolute activities⁹ λ by the relations

$$\log \left(\frac{K_p}{\text{atm.}^{-1}} \right) = - \frac{\Delta G^\dagger}{RT} = - \frac{\mu_{\text{C}_2\text{H}_6}^\dagger - \mu_{\text{C}_2\text{H}_4}^\dagger - \mu_{\text{H}_2}^\dagger}{RT} = - \log \left(\frac{\lambda_{\text{C}_2\text{H}_6}^\dagger}{\lambda_{\text{C}_2\text{H}_4}^\dagger \lambda_{\text{H}_2}^\dagger} \right), \quad (2, 3)$$

$$\frac{d \log (K_p / \text{atm.}^{-1})}{dT} = - \frac{\Delta H}{RT^2} \quad (2, 4)$$

where the operator Δ denotes the increase in the value of any quantity when the reaction (2, 1) takes place from left to right and the superscript \dagger denotes the value at a pressure of one atmosphere.

TABLE I.
CONTRIBUTIONS TO G^\dagger/RT AND TO H/RT .

Freedom.	Contribution to μ^\dagger/RT or to $\log_e \lambda^\dagger$ or to G^\dagger/RT .	Contribution to H/RT .
Translation :	$-7.86 - \log_e \left\{ M^{\frac{3}{2}} \left(\frac{T}{100 \text{ deg.}} \right)^{\frac{3}{2}} \right\}$	2.50
Rotation : (linear molecule).	$-0.925 - \log_e \left\{ \frac{A}{10^{-40} \text{ g. cm.}^2} \cdot \frac{T}{100 \text{ deg.}} \frac{1}{\sigma} \right\}$	1.00
Rotation : (non-linear molecule).	$-1.96 - \log_e \left\{ \frac{(ABC)^{\frac{1}{2}}}{(10^{-40} \text{ g. cm.}^2)^{\frac{3}{2}}} \left(\frac{T}{100 \text{ deg.}} \right)^{\frac{3}{2}} \frac{1}{\sigma} \right\}$	1.50
Internal vibration.	$-\log_e (1 - e^{-\Theta_v/T})$	$\frac{\Theta_v/T}{e^{\Theta_v/T} - 1}$
Internal free rotation.	$\left\{ -1.04 - \log_e \left(\frac{I}{10^{-40} \text{ g. cm.}^2} \right)^{\frac{1}{2}} \left(\frac{T}{100 \text{ deg.}} \right)^{\frac{1}{2}} \frac{1}{\sigma_1} \right\}$	0.50
Zero energy.	E_0/RT	E_0/RT

⁸ Kemp and Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 276.

⁹ For definition see Fowler and Guggenheim, *Statistical Thermodynamics* (1939), p. 66 and p. 192 footnote.

According to statistical mechanics, the contributions of the various degrees of freedom to G^\dagger , μ^\dagger and H are additive, and can be calculated by standard formulæ.¹⁰ These are conveniently used in the numerical forms collected in Table I, in which the symbols have the following meanings. M is the molecular weight on the conventional chemical scale. A , B , C are principal moments of inertia; σ is a symmetry number defined as the number of indistinguishable orientations of the molecule regarded as rigid. Θ_v is the frequency of a vibration measured as a temperature; It is related to the wave number ω by $\Theta_v = \hbar c \omega / k$ or $\Theta_v / \text{deg.} = 1.432 \omega / \text{cm.}^{-1}$. I is the reduced moment of inertia and σ_i the symmetry number appropriate to the internal rotation. Finally, E_0 is the energy of the lowest quantum state of the molecule referred to any zero, provided that the three zeros for C_2H_6 , C_2H_4 and H_2 are mutually consistent. Any contributions due to nuclear structure remain unaltered by physico-chemical processes except for the terms in $\log \sigma$, which by convention are included in the rotational contributions.

4. Molecular Constants.

Hydrogen.—In the relevant temperature range it is entirely adequate to treat the hydrogen molecule as a rigid rotator with $M = 2.018$, with $A/10^{-40} \text{ g. cm.}^2 = 0.46$ and with $\sigma = 2$. The effect of quantisation of the rotational motion is,¹¹ in the relevant temperature range, to decrease the classical values of μ^\dagger/R and H/R by the almost constant amount 30 deg., and this correction can be absorbed into E_0/R . There is also a stretching due to centrifugal force, but for the present purpose the effect of this on all the thermodynamic functions is entirely negligible.

Ethylene.—For ethylene $M = 28.03$ and, according to Badger,¹² A , B , C have the values 5.7, 27.5, and 33.2 in units of $10^{-40} \text{ g. cm.}^2$ and $\sigma = 4$. The normal modes as assigned by Bonner¹³ are listed in Table II.

TABLE II.

NORMAL MODES OF ETHYLENE AS ASSIGNED BY BONNER.¹³

Symmetry Class.	Reference * Symbol.	Wave number cm. ⁻¹ .	$\frac{\Theta_v}{100 \text{ deg.}}$	Symmetry Class.	Reference Symbol.	Wave number cm. ⁻¹ .	$\frac{\Theta_v}{100 \text{ deg.}}$
A_{1g}	$\left\{ \begin{array}{l} \nu_2 \\ \nu_4 \end{array} \right.$	3019 1623	43.3 23.25	B_{1g}	$\left\{ \begin{array}{l} \nu_6 \\ \nu_{10} \end{array} \right.$	3069 950	44.0 13.6
	ν_8	1342	19.3		ν_{11}	940	13.45
	ν_7	[000]	[12.9]		ν_{12}	1100	15.75
A_{1u}^\dagger	ν_1	2988	42.8	B_{2g}	$\left\{ \begin{array}{l} \nu_5 \\ \nu_9 \end{array} \right.$	3107 950	44.5 13.6
B_{1u}	ν_3	1444	20.7	B_{2u}			

* These are the symbols used by Sutherland.

† The A_{1u} mode is the twisting mode.

The A_{1u} mode, a twisting of one CH_2 group relative to the other, is completely inactive both in the Raman and infra-red, and its value is

¹⁰ See for example Fowler and Guggenheim, *Statistical Thermodynamics* (1939), henceforth referred to as S.T.

¹¹ S.T., p. 202, footnote.

¹² Badger, *Physic. Rev.*, 1934, 45, 648.

¹³ Bonner, *J. Amer. Chem. Soc.*, 1936, 58, 34.

assigned so as to agree with measurements of heat capacity. Values thus assigned are 803 cm.^{-1} by Eucken and Parts,⁷ 950 cm.^{-1} by Frost,¹⁴ 790 cm.^{-1} by Smith and Vaughan,² and 815 cm.^{-1} by Bonner.¹³ I have used the value $\omega = 900\text{ cm.}^{-1}$ or $\Theta_v = 1290\text{ deg.}$, which seems to fit the heat capacity data as well as any, as has been shown elsewhere.¹⁵

The excellent agreement found by Egan and Kemp¹⁶ between the calorimetric and spectroscopic values of the entropy S^\dagger of the saturated vapour of ethylene at the boiling-point 169.4° K. is independent of the value assumed for the twisting frequency, since at such a low temperature the total contribution of the 12 frequencies to S^\dagger/R is only about 0.015 , which is less than the experimental error.

Ethane.—For ethane $M = 30.05$ and accepting the values of Frost,¹⁴ also used by Teller and Topley,¹ $A = 10.74$, $B = C = 40.09$, $I = 2.68$ all in units of 10^{-40} g. cm.^2 . The symmetry number σ for the molecule regarded as rigid is 6, and the internal symmetry number σ_1 for the mutual rotation of the two methyl groups is 3. Of the 18 normal modes, 17 have been determined spectroscopically either in the infra-red or in the Raman spectrum. The frequencies assigned by Crawford, Avery and Linnett¹⁷ are given in Table III. There have been several previous

TABLE III.
NORMAL MODES OF ETHANE AS ASSIGNED BY CRAWFORD, AVERY AND LINNETT.¹⁷

Single Modes.			Pairs of Modes. (Doubly Degenerate Modes).		
Symmetry Class.*	Wave-number cm. ⁻¹	Θ_v 100 deg.	Symmetry Class.*	Wave-number cm. ⁻¹	Θ_v 100 deg.
A'_1	$\begin{cases} 993 \\ 1375 \\ 2927 \end{cases}$	$\begin{matrix} 14.20 \\ 19.6 \\ 41.9 \end{matrix}$	E'	$\begin{cases} 827 \\ 1480 \\ 2980 \end{cases}$	$\begin{matrix} 11.84 \\ 21.2 \\ 42.6 \end{matrix}$
A'_2	$\begin{cases} 1380 \\ 2926 \end{cases}$	$\begin{matrix} 19.8 \\ 41.9 \end{matrix}$	E''	$\begin{cases} [1120] \\ 1460 \\ 2970 \end{cases}$	$\begin{matrix} [16.0]^\dagger \\ 20.9 \\ 42.5 \end{matrix}$
A''_1	Twisting mode				

* These symmetry classes assume a molecule with a point group D_{2h} . These are all alternative possibilities.

† This is the "uncertain" mode.

assignments, but they are all in essential agreement except with respect to the frequency 1120 cm.^{-1} assigned to one of the doubly degenerate E'' modes. This frequency does not occur as a fundamental either in the infra-red or in the Raman spectrum, and is conveniently referred to as the "uncertain" frequency. The evidence for the value 1120 cm.^{-1} is discussed by the above-mentioned authors, and I have accepted this value. Quite recently Karweil¹⁸ claimed to have spectroscopic evidence for the value 740 cm.^{-1} for this frequency, but he has since admitted¹⁹ the correctness of a value near 1120 cm.^{-1} . The remaining spectroscopically inactive mode of ethane is the twisting mode.

¹⁴ Frost, *Compt. rend. U.S.S.R.*, 1933, 161.

¹⁵ S.T., p. 116.

¹⁶ Egan and Kemp, *J. Amer. Chem. Soc.*, 1937, 59, 1264.

¹⁷ Crawford, Avery and Linnett, *J. Chem. Physics*, 1938, 6, 682.

¹⁸ Karweil, *Z. physikal. Chem., B*, 1938, 39, 1.

¹⁹ Karweil and Schäfer, *Z. physikal. Chem., B*, 1938, 40, 382.

As in the case of ethylene, its nature is determined by experimental data on heat capacities. As already mentioned in § 1, the experimental data throughout the temperature range 90° K. to 300° K. can be fitted by assuming the twisting (or internal rotation) to have a potential energy u of the form

$$u = u_0 \sin^2 \left(\sigma_1 \frac{\phi}{2} \right), \quad (3, 1)$$

with maximum u_0 determined by $u_0/k = 1570$ deg., and with internal symmetry number $\sigma_1 = 3$. This assumption is in excellent agreement,²⁰ not only with the recent measurements at low temperatures by Kistiakowsky and Nazmi,⁵ and by Hunsmann,⁶ but also with the previous measurements at higher temperatures by Eucken and Parts,⁷ and with the much earlier measurements by Heuse.⁴

4. Thermodynamic Functions.

The results of calculations of ΔH and of $\log K_p$ are summarised in Tables IV and V respectively. The calculations are based on the

TABLE IV.
CONTRIBUTIONS TO $\Delta H/RT$ AND VALUES OF $-\Delta H$.

Temperature $\left\{ \begin{array}{l} ^\circ\text{C.} \\ ^\circ\text{K.} \end{array} \right.$	82. 355.	400. 673.	500. 773.	600. 873.	700. 973.
Hydrogen	3.50	independent of temperature.			
Ethane — ethylene : Translation + rotational . .	0.00				
Ethylene :					
11 certain modes	0.36	1.65	2.06	2.45	2.83
Twisting mode	0.10	0.33	0.39	0.44	0.48
Total vibrational	0.46	1.98	2.45	2.89	3.31
Ethane :					
15 certain modes	0.43	2.00	2.53	3.04	3.54
Pair of "uncertain" modes .	0.10	0.48	0.60	0.70	0.79
Internal free rotation . . .	0.50	0.50	0.50	0.50	0.50
Effect of restriction	0.10	0.29	0.29	0.29	0.29
Total vibrational	1.13	3.27	3.92	4.53	5.12
$-(\Delta H - \Delta E_0)/RT$. . .	2.83	2.21	2.03	1.86	1.69
$-(\Delta H - \Delta E_0)/10^3 R$ deg. .	1.00	1.49	1.57	1.62	1.65
$-\Delta E_0/10^3 R$ deg. . . .	15.52	15.52	15.52	15.52	15.52
$-\Delta H/10^3 R$ deg. . . .	16.52*	17.01	17.09	17.14	17.17

* Experimental value of Kistiakowsky et al.²²

formulae given in Table I and the molecular constants specified in § 3. The contributions made by the translation and by the rotation to $\Delta H/RT$ and to $\log K_p$ differ in the case of ethane, and in the case of ethylene by amounts independent of the temperature, and it is therefore convenient to tabulate only this difference. The contributions of the 11 certain modes of ethylene and of the 15 certain modes of ethane have been lumped together, but the contributions of the twisting mode of ethylene, of the pair of "uncertain" modes of ethane and of the twisting

²⁰ S.T., p. 118, where references are given.

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TABLE V.

CONTRIBUTIONS TO $-\Delta G^\dagger/RT = \log_e K_p$ AND VALUES OF K_p .

Temperature { °C. °K.	78. 355.	400. 673.	450. 723.	500. 773.	550. 823.	600. 873.	650. 923.	700. 973.
Hydrogen :								
Translation . .	12.08	13.68	13.86	14.02	14.18	14.33	14.47	14.60
Rotation . . .	0.73	1.36	1.44	1.51	1.57	1.63	1.68	1.74
Total	12.81	15.04	15.30	15.53	15.75	15.96	16.15	16.34
Ethane — ethylene :								
Translation . .	0.10	} independent of temperature.						
Rotation . . .	0.20							
Translation + rotation . . .	0.30							
Ethylene :								
11 certain modes .	0.08	0.67	0.80	0.93	1.07	1.21	1.35	1.49
Twisting mode . .	0.03	0.16	0.18	0.21	0.23	0.26	0.28	0.31
Total vibrational .	0.11	0.83	0.98	1.14	1.30	1.47	1.63	1.80
Ethane :								
15 certain modes .	0.11	0.81	0.96	1.12	1.29	1.45	1.63	1.81
Pair of "uncertain" modes	0.02	0.20	0.23	0.27	0.31	0.35	0.39	0.43
Internal free rotation	1.06	1.38	1.42	1.45	1.48	1.51	1.54	1.57
Effect of restriction	-0.67	-0.53	-0.51	-0.49	-0.47	-0.45	-0.44	-0.42
Total vibrational .	0.52	1.86	2.10	2.35	2.61	2.86	3.12	3.39
Ethane—ethylene —hydrogen . .	-12.10	-13.71	-13.89	-14.02	-14.16	-14.27	-14.37	-14.45
$-\Delta E_0/RT$. .	43.71	23.06	21.47	20.08	18.86	17.78	16.81	15.95
$-\Delta G^\dagger/RT =$ $\log_e (K_p/\text{atm.}^{-1})$.	31.61	9.35	7.58	6.06	4.70	3.51	2.44	1.50
$K_p/\text{atm.}^{-1}$ calc. .	—	1.1×10^4	2.0×10^3	4.3×10^2	1.1×10^2	34	11.5	4.5

mode (internal rotation) of ethane have been listed separately, so as to facilitate revision of the computations in the future by anyone who may have obtained improved data. The contributions of the twisting mode of ethane have been computed as those of free rotation diminished by a correction term estimated by interpolation of the tables prepared by Pitzer.²¹ Finally, the value of the unknown quantity ΔE_0 has been chosen so as to agree exactly with the experimental value $-\Delta H/R = 16.52 \times 10^3$ deg. at 355° K. obtained by Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan.²²

5. Comparison with Experiment.

As already mentioned, the value of ΔE_0 has been chosen so as to give exact agreement with the experimental value of Kistiakowsky *et al.* of $-\Delta H$ at 355° K. The test of the agreement between theory and experiment is therefore confined to a comparison of calculated and observed values of K_p . This comparison is summarised in Table VI.

²¹ Pitzer, *J. Chem. Physics*, 1937, **5**, 469.

²² Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan *J. Amer. Chem. Soc.*, 1935, **57**, 65.

TABLE VI.

COMPARISON OF CALCULATED AND OBSERVED VALUES OF K_p .

Temperature.		$K_p/\text{atm.}^{-1}$ calc.	$K_p/\text{atm.}^{-1}$ measured.*			
° C.	° K.		P.D.	T.P.	F.H.	V.V.
700	973	4.5	5.0	—	—	—
650	923	11.5	12.2	12.7	—	—
630	903	17.5	—	18.5	—	—
620	893	21.5	—	22.4	—	—
610	883	27	—	27.5	—	—
600	873	33.5	32	—	—	—
590	863	41	—	41	—	—
570	843	67	—	60 and 65	—	—
550	823	1.1×10^3	—	1.35×10^3 †	—	—
500	773	4.3×10^3	—	—	4.2×10^2	3.2×10^3
450	723	2.0×10^3	—	—	1.8×10^3	—
400	673	1.1×10^4	—	—	1.2×10^4	—

References : * P.D. Pease and Durgan.²³T.P. Travers and Pearce.²⁴F.H. Frey and Huppke,²⁵ reinterpreted by Kistiakowsky.²²V.V. Videnski and Vinikova.²⁶† According to Teller and Topley,¹ the experimental method used here is unreliable at such a low temperature.

Where necessary, calculated values have been interpolated by use of formulæ (6, 1) of the following section. The experimental data of the various workers have been tabulated by Teller and Topley,¹ and I have taken the values from their table. As regards the measurements of Frey and Huppke,²⁵ I have accepted the reinterpretation of their data by Kistiakowsky.²²

It will be seen from the table that the disagreement between calculated and observed values of K_p is less than 10 %, with the single exception of the data of Videnski and Vinikova,²⁶ where the discrepancy is about 35 %. Thus the agreement may be considered complete within the accuracy of both calculation and experiment. In fact, in my opinion, the excellence of the agreement may well be partly fortuitous.

6. Interpolation Formulæ.

Throughout the temperature range 763° K. to 973° K. the results of the calculations can be expressed by the formulæ

$$\log_e \left(\frac{K_p}{\text{atm.}^{-1}} \right) = - \frac{\Delta G^\dagger}{RT}$$

$$= 15.52 \frac{10^3 \text{ deg.}}{T} - 16.20 + 3.35 \log_e \left(\frac{10^3 \text{ deg.}}{T} \right) + 1.70 \frac{T}{10^3 \text{ deg.}}, \quad (6, 1)$$

$$- \frac{\Delta H}{R 10^3 \text{ deg.}} = 15.52 + 3.35 \frac{T}{10^3 \text{ deg.}} - 1.70 \left(\frac{T}{10^3 \text{ deg.}} \right)^2, \quad (6, 2)$$

$$- \frac{\Delta C_p}{R} = 3.35 - 3.40 \frac{T}{10^3 \text{ deg.}}, \quad (6, 3)$$

²³ Pease and Durgan, *J. Amer. Chem. Soc.*, 1928, 50, 2715.²⁴ Travers and Pearce, *J. Soc. Chem. Ind.*, 1934, 53, 322.²⁵ Frey and Huppke, *Ind. Eng. Chem.*, 1933, 25, 54.²⁶ Videnski and Vinikova, *J. Gen. Chem. Moscow*, 1934, 4 [46], 120.

where C_p denotes heat capacity at constant pressure. These formulae reproduce the calculated values and, so also the smoothed experimental values, with an accuracy better than 0.01 in $\log_e K_p$ and in $-\Delta H/RT$ or an accuracy of 1 % in K_p , which is more than sufficient. The formulae are designed for interpolation only, and should not be used without caution outside the range 673° K. to 973° K. Actually, at 355° K. formula (6, 2) leads to the value 16.50 for $-\Delta H/R10^3 \text{ deg.}$ as compared with the accepted value 16.52, so that the use of (6, 2) for extrapolation over a considerable temperature range would appear permissible.

According to (6, 3) $\Delta C_p/R$ vanishes and $-\Delta H$ has a maximum at $T = 985^\circ \text{ K.}$ Consequently, ΔH happens to be varying especially slowly at temperatures not too far removed from 985° K. As a result of this, K_p can be calculated throughout the range 673° K. to 973° K. by the simpler formula

$$\log_e \left(\frac{K_p}{\text{atm.}^{-1}} \right) = -\frac{\Delta G^\ddagger}{RT} = 17.10 \frac{10^3 \text{ deg.}}{T} - 16.07 \quad (6, 4)$$

As far as concerns values of K_p , this formula is practically as accurate as (6, 1), but the inaccuracy is magnified by differentiation, so that the derived formula

$$-\Delta H/R10^3 \text{ deg.} = 17.10 \quad (6, 5)$$

is appreciably less accurate than (6, 2) and from it one can obtain no information concerning ΔC_p .

From the above it is clear that an interpolation formula which fits with high accuracy for K_p , may lead to inaccurate values of ΔH obtained by differentiation, and to entirely spurious values of ΔC_p obtained by a second differentiation. One should therefore regard with caution values of ΔC_p obtained entirely from experimental measurements of K_p . This remark may possibly be relevant in connection with ΔC_p values derived in this manner for certain acid-basic equilibria.²⁷

7. Entropy of Ethane.

In the course of the calculations described above, I have tried to check numerical formulae of Table I against calculated values of thermodynamic functions published by other authors. In the cases of hydrogen and ethylene I have found complete agreement, but in the case of ethane there is a small but not negligible discrepancy between some of my calculated values and those published by Kemp and Pitzer.⁸ As these authors give insufficient details of their calculations, I am unable to trace the cause of these small discrepancies. I accordingly include tables of the various contributions to the thermodynamic functions of ethane at the three temperatures 184° K., 298° K., and 355° K. at which Kemp and Pitzer have calculated the entropy. These calculations are summarised in Table VII. The contributions to H and μ^\ddagger are calculated by the formulae of Table I, and then contributions to S^\ddagger the entropy at one atmosphere are derived by the relation

$$S^\ddagger = (H - \mu^\ddagger)/T \quad (7, 1)$$

It is curious that the values obtained by Kemp and Pitzer for a molecule with free internal rotation differ appreciably from my values, and yet their final values corrected for the restricting rotational potential

²⁷ Cf. Everett and Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35**, 1380.

TABLE VII.

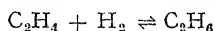
CONTRIBUTIONS TO THERMODYNAMIC FUNCTIONS OF ETHANE.

	$H/RT.$	$-\mu^\dagger/RT$	$S^\dagger/RT.$	$S^\dagger/\text{cal. deg.}^{-1}.$		
				E.A.G.	K. & P. ⁵	Expt. ²⁸
355° K.						
Translation + rotation	4.00	23.07	27.07	—	—	—
17 vibrations	0.53	0.13	0.66	—	—	—
Internal free rotation	0.50	1.06	1.56	—	—	—
Sum	5.03	24.26	29.29	58.17	58.74 ?	—
Effect of restriction	0.10	-0.67	-0.57	-1.13	—	—
Resultant	5.13	23.59	28.72	57.04	57.06	—
298° K.						
Translation + rotation	4.00	22.37	26.37	—	—	—
17 vibrations	0.30	0.06	0.36	—	—	—
Internal free rotation	0.50	0.98	1.48	—	—	—
Sum	4.80	23.41	28.21	56.03	56.36 ?	—
Effect of restriction	0.04	-0.69	-0.65	-1.29	—	—
Resultant	4.84	22.72	27.56	54.74	54.62	—
184° K.						
Translation + rotation	4.00	20.45	24.45	—	—	—
17 vibrations	0.03	0.00	0.03	—	—	—
Internal free rotation	0.50	0.74	1.24	—	—	—
Sum	4.53	21.19	25.72	51.09	51.09	—
Effect of restriction	-0.20	-0.64	-0.84	-1.67	—	—
Resultant	4.33	20.55	24.88	49.42	49.30	49.54

energy agree reasonably well. The explanation that suggests itself is that the error is one of transcription rather than of calculation.

Summary.

The equilibrium constant K_p for the reaction



has been calculated by the methods of statistical mechanics. In the calculation use is made of spectroscopic data (Raman and infra-red), of measurements of heat capacity and of a single measurement of the heat of reaction, but no use is made of any data relating to the equilibrium of the above reaction. The calculated values of K_p are compared with the experimental values of four sets of authors extending over the range of temperatures 673° K. to 973° K. The agreement between calculation and experiment is complete, better than 10 % in K_p except for one experimental value. The results of the calculations as well as the smoothed experimental data can be represented accurately by the formulæ:—

$$\log_e \left(\frac{K_p}{\text{atm.}^{-1}} \right) = 15.52 \frac{10^3 \text{ deg.}}{T} - 16.20 + 3.35 \log_e \left(\frac{10^3 \text{ deg.}}{T} \right) + 1.70 \frac{T}{10^3 \text{ deg.}},$$

$$-\frac{\Delta H}{R \cdot 10^3 \text{ deg.}} = 15.52 + 3.35 \frac{T}{10^3 \text{ deg.}} - 1.70 \left(\frac{T}{10^3 \text{ deg.}} \right)^2,$$

valid throughout the experimental temperature range 673° K. to 973° K.

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²⁸ Witt and Kemp, *J. Amer. Chem. Soc.*, 1937, **59**, 273.

THE ABSORPTION SPECTRA OF NITROGEN DIOXIDE, OZONE AND NITROSYL CHLORIDE IN THE VACUUM ULTRA-VIOLET.

BY W. C. PRICE AND MISS D. M. SIMPSON.

Communicated by R. G. W. NORRISH.

It has been known for some time that triatomic molecules which possess sixteen 'molecular electrons' (that is, electrons derived from the outer atomic shells) have a linear structure. Examples of such molecules are carbon dioxide, nitrous oxide, the cyanogen halides, and the ions NCO^- , NCS^- , BO_2^- , N_3^- , etc. According to the molecular orbital theory, this phenomenon is due to the fact that for linear symmetry the maximum number of electrons which can be accommodated in bonding or non-bonding orbitals is sixteen.¹ The only orbitals into which a seventeenth electron can go are of a strongly anti-bonding nature.* To avoid this, the molecule becomes bent, and thus acquires a new set of molecular orbitals appropriate to the new symmetry. From the point of view of bond formation the important difference between linear and bent molecules is that in the former class the 's' orbitals of the central atom are used for bond orbitals whereas in the bent triatomic molecules these are occupied by an unshared pair of electrons, and it is the 'p' atomic orbitals which are employed in the formation of the primary single bonds. For example in carbon dioxide, the valence configuration of the carbon is ' sp^3 ', the structure of the basic or bond orbitals being ' sp ' (i.e., $\frac{1}{\sqrt{2}}(s + p_x)$ and $\frac{1}{\sqrt{2}}(s - p_x)$). On the other

hand, in molecules such as nitrogen dioxide, sulphur dioxide and chlorine dioxide, the basic single bond orbitals of the central atom are 'p' orbitals. These orbitals are mutually perpendicular, although in practice the apical angle deviates from 90° , because of electrostatic repulsion and other effects. The increase of strength in the binding of the 's' shell, in going up the periodic table, is probably partly responsible for the withdrawal of this shell from participation in bond formation. The present work was undertaken in the hope that the absorption spectra of these bent triatomic molecules might give some information about their electronic structure.

Nitrogen Dioxide.

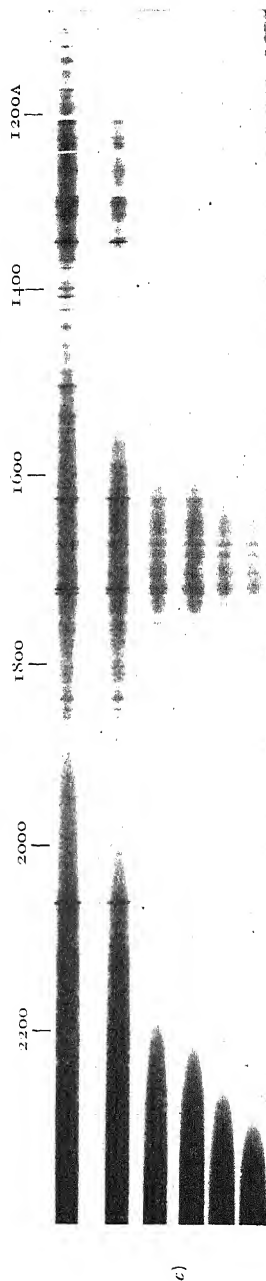
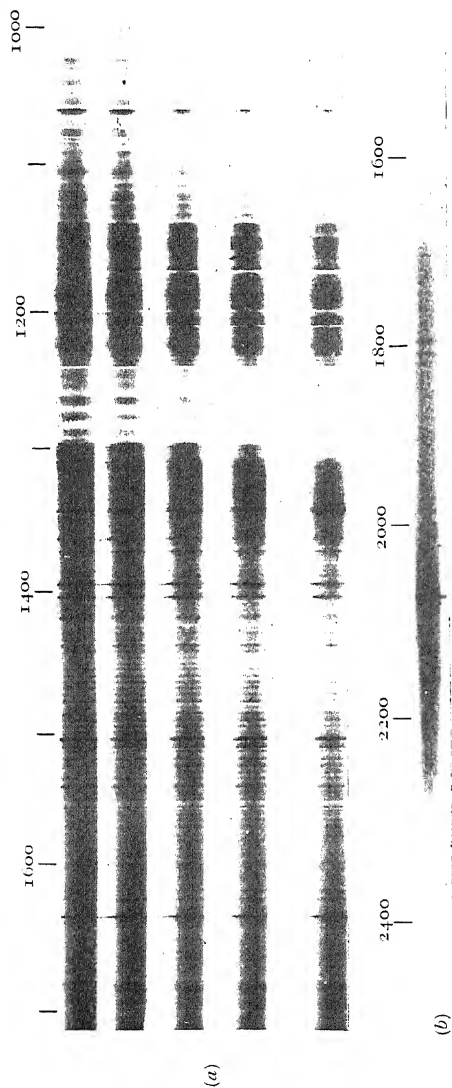
The absorption spectra in the vacuum ultra-violet of some of the 'sixteen electron' molecules have already been published.†² The first

¹ R. S. Mulliken, *J. Chem. Physics*, 1935, 3, 720.

* The analogous phenomenon for diatomic molecules occurs in the case of nitrogen and nitric oxide.

† A report on the spectra of the cyanogen halides is also to be published shortly.

² (a) A. B. F. Duncan, *ibid.*, 1936, 4, 638; (b) W. C. Price and D. M. Simpson, *Proc. Roy. Soc., A*, 1938, 165, 272; (c) W. C. Price and D. M. Simpson, *ibid.*, 1939, 169, 501.



(a) Nitrogen dioxide. (b) Ozone. (c) Nitrosyl chloride.

of the molecules with more than sixteen 'molecular electrons' to be considered is nitrogen dioxide. This molecule has a large variety of absorption bands in the visible and near ultra-violet; however those in the vacuum ultra-violet are by far the strongest (Plate I (a)). The absorption in this region occurs below 1600 Å, and appears at pressures of a few hundredths of a millimetre in a path length of one metre (this is equivalent to complete absorption in passing through a few hundredths of a millimetre of gas at N.T.P.). From the reproduction it can be seen that the absorption consists of a very large number of sharp bands, which are slightly degraded towards the red. They start relatively weakly around 1580 Å, increase to a maximum about 1450 Å, and the intensity then diminishes more rapidly, the bands continuing to about 1350 Å on the short wavelength side. The main heads of some fifty of the bands can be arranged in a very plausible vibrational progression with a frequency difference of about 200 cm^{-1} (Table I). They are accompanied by slightly weaker sub-heads occurring about 75 cm^{-1} on the long wavelength side. These sub-heads can be arranged in a similar series with roughly the same frequency separation. Such a vibrational analysis, over the very wide range of wavelengths from 1550–1350 Å, implies that we are dealing with only one electronic transition, or possibly two electronic transitions very close together. This interpretation is in agreement with the intensity variation, which increases continuously to a maximum, and then diminishes to zero in traversing this region.

The most acceptable assignment of the 200 cm^{-1} frequency difference is to the $\delta_e ||$ (or γ_2) deformation vibration, which has a value of 640 cm^{-1} in the ground state. This agrees with the usual diminution in frequency on excitation, and with the vibrational selection rules. A long vibrational progression of this type involving

TABLE I.—BANDS IN THE 1600–1400 Å. SYSTEM OF NITROGEN DIOXIDE.

I.	ν cm^{-1} .	$\Delta\nu$.
I	63125	—
I	63335	210
I	63545	210
I	63730	185
2	63940	210
2	64120	180
3	64300	180
3	64540	240
3	64740	200
3	64940	200
4	65130	190
4	65350	220
4	65540	190
5	65725	185
5	65945	220
6	66150	205
6	66330	180
6	66550	220
7	66740	190
7	66920	180
6	67135	215
6	67355	220
8	67555	200
8	67755	200
8	67955	200
9	68145	190
8	68340	195
8	68545	205
7	68750	205
8	68950	200
8	69150	200
6	69345	195
6	69550	205
7	69730	180
4	69955	225
4	70160	205
4	70340	180
3	70505	165
3	70750	245
2	70940	190
2	71140	200
3	71335	195
3	71545	210
2	71950	2 × 203
I	72135	185
I	72320	185
I	72535	215

Average 200 cm^{-1} .

the deformation frequency is to be expected, if the $\angle \text{ONO}$ angle changes considerably in going from the ground to the excited state. The

intensity distribution of the absorption, with its maximum close to the short wavelength end of the system, supports this hypothesis. The weaker progression observed at 75 cm.^{-1} to the long wavelength side of the strong 1550–1350 Å progression appears to arise from another upper electronic state very close to the first. It cannot be due to any doublet separation in the ground state which is analogous in character to a ${}^2\Sigma$ state in diatomic molecules. This is indicated by the fact that the whole of the magnetic susceptibility of nitrogen dioxide can be attributed to the spin of the odd electron.³ No contribution from orbital angular momentum is observed, a result which seems to be true of all polyatomic molecules.⁴ The thermodynamic data obtained by Giaque and Kemp⁵ also indicates that the ground state of nitrogen dioxide must be of a ${}^2\Sigma$ character. Reasons will be given later for attributing the 1550–1350 Å band system to the excitation of one of the double bond ' π ' electrons.

To shorter wavelengths, 1290–1260 Å, a new electronic transition of a quite different character occurs. It consists of five strong and rather diffuse bands with a frequency separation of about 610 cm.^{-1} (Table II).

TABLE II.

BANDS IN THE 1280 AND 1135 Å PROGRESSIONS OF NITROGEN DIOXIDE.

1280 Å Progression.			1135 Å Progression.		
I.	$\nu \text{ cm.}^{-1}$.	$\Delta\nu$.	I.	$\nu \text{ cm.}^{-1}$.	$\Delta\nu$.
6	77360	—	5	87470	—
10	77970	610	1	88020	550
8	78580	610	2	88580	560
4	79180	600	3	89140	560
	Average	610	—	Average	560

Since the amount of vibrational structure accompanying this transition is limited, there is no great change in the molecular constants. It is therefore reasonable to interpret the 610 cm.^{-1} frequency difference as a slightly diminished $\delta_z ||$ or ν_2 vibration, which is 640 cm.^{-1} in the ground state. A second similar group of bands appears in the region 1150–1120 Å. Its members are rather overlaid with emission lines, and it is difficult to measure them very accurately, but they seem to correspond to a single progression with a mean frequency difference of 560 cm.^{-1} . The appearance of the two band groups near 1280 and 1135 Å is quite different from those at longer wavelengths, and their resemblance to each other suggests that they may be the successive members of a Rydberg series. If this is so, then they would correspond to an ionization potential of about 12.3 v.

$$\nu_0^n = 99,500 - R/(n + 0.25)^2 \quad n = 2, 3, \dots$$

The third and probably the fourth members of this series could be observed, but a background of continuous absorption prevented very

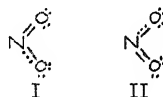
³ G. G. Havens, *Physic. Rev.*, 1932, **41**, 337.

⁴ R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge University Press, 1939, p. 631.

⁵ W. F. Giaque and J. D. Kemp, *J. Chem. Physics*, 1938, **6**, 40.

accurate measurements being made on them. The error in the extrapolation is of the order of a fifth of a volt. The series is very similar in appearance to one in sulphur dioxide going to an ionization potential ^{2(a)} of 12.05 v., and to the AB series in water with an ionization potential ⁶ of 12.56 v. In all these cases the electron is apparently removed without much change in angle, and no frequency differences were found which could be attributed to valence vibrations. Thus the electron excited must be relatively non-bonding. It is probably more or less localised on the oxygen atom, the magnitude of the ionization potential indicating it to be a $2p\pi[\text{O}]$ electron.

The electronic formula of nitrogen dioxide which is in best agreement with its chemical behaviour, bond distances and vibrational frequencies, is considered by Pauling ⁷ to be embodied in the resonating structures I and II. One oxygen atom is held to the nitrogen by a double bond, and the other by a single bond plus a three-electron bond. The



value of 140° for the ONO angle has been deduced by Pauling ⁷ from the entropy measurements of Giauque and Kemp.⁵ The electrons in the above formula which correspond to the lowest ionization potential are probably the ' $2p$ ' non-bonding electrons of the oxygen atoms ($2p\pi[\text{O}]$). These have their symmetry axes in the ONO plane and perpendicular to the ON bonds. The molecule can be considered as having a saturated 'in plane' configuration of molecular orbitals with one ' π ' electron at each of the three atoms perpendicular to the molecular plane. It appears that the removal of the unpaired electron does not correspond to the minimum ionization of the molecule, as it does in nitric oxide. The heat of formation of nitrogen dioxide from its constituent atoms has the relatively large value of 195.3 K.cal., which is only 15 Kcal. less than nitrous oxide. This indicates that the odd ' π ' electron with its axis perpendicular to the molecular plane must contribute to the bonding, and thus may be expected to have a higher ionization potential than that of the non-binding oxygen electrons, which are only paired in the atomic sense. The small dipole moment ⁸ of the molecule [0.4 ± 0.1 D.] shows only a slight excess of negative charge on the oxygen atoms. This would explain why the ionization potential of the non-bonding ' $2p$ ' oxygen electrons is somewhat less than would otherwise be expected. Mulliken ⁹ gives the theoretical value of 14.73 v. for this ionization potential which is calculated on the assumption that there is no change in the charge on the oxygen atom when it is in combination.

Because of the limited vibrational structure accompanying the upper electronic states, it is clear that the ionization potential of nitrogen

dioxide at 12.3 v. corresponds to a state of NO_2^+ in which the ONO angle is not very different from that in the normal state of the molecule. It might be expected that the lowest state of NO_2^+ would be linear, since the ion is iso-electronic with carbon dioxide. But, from the Franck-Condon Principle, it is unlikely that photo-ionization to such a state

⁵ W. C. Price, *J. Chem. Physics*, 1936, 4, 147.

⁷ L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, 1939, p. 250.

⁸ C. T. Zahn, *Physik. Z.*, 1933, 34, 461.

⁹ R. S. Mulliken, *J. Chem. Physics*, 1934, 2, 782.

could be observed. Possibly the ionization potential of 11 ± 1 v. observed by electron impact¹⁰ corresponds to an excitation to this state, but the inaccuracy of the determination prevents its being used as the basis of any argument. We have made independent electron impact determinations of the ionization potential and obtain a value agreeing with that deduced from the Rydberg formula to within 0.1 v.

The system in the neighbourhood of 2500 Å has recently received considerable attention. Harris, King, Benedict and Pearse¹¹ give a vibrational analysis of the bands which requires that the electronic transition starts from a vibrating ground state having at least one quantum of the 640 cm^{-1} vibration. The two former authors¹² also present a rotational analysis of the 2491 Å band from which they deduce a value

of $154 \pm 4^\circ$ for the ONO angle and 1.28 ± 0.03 Å for the NO distance. These results disagree with the electron impact determinations of Maxwell

and Mosley¹³ who get $130 \pm 2^\circ$ for the ONO angle and 1.21 ± 0.02 Å for the NO distance.

To the long wavelength side of the bands at 1280 and 1135 Å there occur weak diffuse bands due to transitions from vibrating ground states. The separations of these from the ν_0 bands are between 600 and 650 cm^{-1} but the diffuseness of the bands and overlapping emission lines prevents a more accurate determination being made.

Sulphur Dioxide and Ozone.

A detailed report of the absorption spectrum of sulphur dioxide has already been published.^{2(b)} In order to compare it with the spectrum of ozone, nitrogen dioxide and nitrosyl chloride, a brief summary of its main features is given here. The absorption band systems of sulphur dioxide can be roughly divided into two classes (1) those which exhibit wide vibrational structure, (2) those which show little or no vibrational structure. The former class probably corresponds to transitions to anti-bonding orbitals associated with an electronic configuration not differing greatly, if at all, from that of the ground state. The latter type is due to transitions of comparatively non-bonding electrons to excited orbitals which are mainly atomic (Rydberg) in character. The first three systems of bands, lying at 3200–2600 Å, 2300–1800 Å, and 1580–1520 Å respectively, probably belong to the first class. They appear to involve mainly

vibrations in the OSO angle, and may be interpreted in a way similar to that suggested for the 1550–1350 Å bands in nitrogen dioxide. The 3200–2600 Å system has a maximum molecular extinction coefficient of the order¹⁴ of 400; the 2300–1800 Å bands are several times stronger, and the 1580–1520 Å set is slightly weaker than the first of these. At shorter wavelengths (less than about 1350 Å) the bands are quite different and are classified as type (2). They show little vibrational structure, and can be interpreted as Rydberg systems converging to an ionization potential at 12.05 v. The absence of much vibrational structure indicates that the value of the OSO angle in the molecular ion is not very

¹⁰ H. P. Smyth and E. C. G. Stückelberg, *Physic. Rev.*, 1930, **36**, 478.

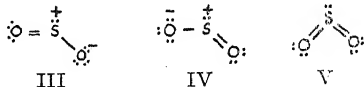
¹¹ Harris, King, Benedict and Pearse, *J. Chem. Physics*, 1940, **8**, 765.

¹² Harris and King, *ibid.*, 775.

¹³ L. R. Maxwell and V. M. Mosley, *ibid.*, 738.

¹⁴ C. S. Garrett, *J. Chem. Soc.*, 1915, 1324.

different from that in the normal molecule (that is, about 120°). The electron ionized can be regarded as belonging to a lone pair of '2p' electrons located on the oxygen atom. The electronic configuration of sulphur dioxide is usually represented by the resonating pair of structures III and IV. Each oxygen is joined to the sulphur by a 'σ' orbital involving one of the 'p' orbitals of the sulphur atom. In addition to these primary single bonds there is a π bond which cannot be localised.



The orbital of this is formed by a suitable combination of the 'p_x' orbitals of the sulphur and oxygen atoms, that is from the 'p' orbitals perpendicular to the OSO plane. Kimball¹⁶ considers that the structure V is as important as the pair given above. In this configuration one of the '3d' sulphur orbitals acts as an acceptor for one of the electron pairs from the oxygen atom. Such a structure could not occur in ozone, as there are no 'd' orbitals in the L shell which could be used. This is no doubt partially responsible for the great difference in stability of these two iso-electronic molecules. The differences in their electronic structure are also apparent from their absorption spectra. In sets of iso-electronic molecules such as the methyl halides, or water and hydrogen sulphide, similarities in the characteristic features of their absorption spectra are usually easily recognisable, the spectra of the molecule containing the heavier atom is shifted to longer wavelengths. The electron responsible for the absorption in the iso-electronic pair ozone and sulphur dioxide, is probably, in both cases, a '2p' oxygen electron or a 'π' bonding electron. In comparing the spectra, the only change which might be expected, would be a slight displacement of the sulphur dioxide bands to longer wavelengths relative to those of ozone, resulting from a small excess negative charge on the oxygen atoms of the former molecule. Actually it is very difficult to establish any similarities at all between the absorption spectra of these two molecules. Sulphur dioxide is transparent down to a wavelength of about 3300 Å, but ozone absorbs in the visible,¹⁷ the bands there being responsible for the deep blue colour of liquid ozone. The visible ozone bands are however weak ($\epsilon_{\text{max.}} = 1.12$), and it would therefore seem more plausible to relate the main system of ozone,¹⁷ occurring in the region 2900–2300 Å, with the 3200–2600 Å bands of sulphur dioxide. On the other hand, the strength of this absorption in ozone is more comparable with that of the 2300–1800 Å system in sulphur dioxide, the maximum absorption coefficients of both having about the same value.

The photograph of the absorption spectrum of ozone taken with the vacuum spectrograph (Plate I (b)) is rather disappointing. It shows the short wavelength side of the main system; then the absorption fades out below 2300 Å, and there is a region of relative transparency to 1600 Å. Below this wavelength absorption due to oxygen formed by photo-dissociation prevents any further investigation of that arising from ozone. However, the photograph does indicate that ozone has no strong absorption bands in the region 2300–1600 Å.

¹⁵ V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, 1940, 62, 1270.

¹⁶ G. E. Kimball, *J. Chem. Physics*, 1940, 8, 188.

¹⁷ M. G. Colange, *J. Physique Rad.*, (VI), 1927, 8, 254.

¹⁸ O. R. Wulf and E. M. Melvin, *Physic. Rev.*, 1931, 38, 330.

Nitrosyl Chloride.

Nitrosyl chloride like sulphur dioxide and ozone, belongs to the class of molecules which have eighteen outer electrons. Electron diffraction evidence¹⁹ indicates that the nitrogen lies between the oxygen and chlorine atoms, and that the molecule has a wide-angled structure ($\text{ONCl} \sim 125^\circ$). This is supported by the chemical evidence, and by results obtained from the infra-red and Raman spectra. The absorption in the visible and the near ultra-violet has recently been discussed by Goodeve and Katz.²⁰ The present work is concerned with the much stronger absorption occurring in the vacuum ultra-violet (Plate I (c)). The first region has a maximum at about 1900 Å, which is unsymmetrically located towards the short wavelength side of the system. It resembles the 1550–1350 Å system in nitrogen dioxide, and the 2300–1800 Å system in sulphur dioxide; the maximum extinction coefficient is greater than 2000. The transitions involved are to a high part of the upper potential energy curve, and must produce a considerable change in the size and shape of the molecule. Another strong diffuse system occurs in the region 1600–1350 Å. To shorter wavelengths continuous absorption prevents further investigation of the spectrum. On considering the structures between which nitrosyl chloride resonates, it is probable that the minimum ionization potential of the molecule corresponds to the non-bonding oxygen or chlorine electrons, and that it will have a value between 12 and 13 v.

The absorption spectrum of chlorine dioxide has also been photographed with the vacuum spectrograph. It is entirely continuous extending at low pressures from 1550 Å to shorter wavelengths with a maximum around 1400 Å. With increasing pressures the former limit extends progressively to longer wavelengths. The absorption in the near ultra-violet is particularly interesting because of its great intensity²¹ (ϵ_{max} , at least 2000).

One of the common characteristics of the molecules so far considered, is that they each have a band system with a wide vibrational structure, which appears very intensely in absorption (ϵ about 2000). It seems possible that there may be some analogy between the nitrogen dioxide bands, λ_{max} . 1450 Å, the ozone system λ_{max} . 2550 Å, and those of chlorine dioxide λ_{max} . 3300 Å. This hypothesis receives a certain amount of support from the way in which the heats of formation of the molecules diminish as the bands shift to the red (Table III). This would be in accordance with the interpretation of the bands as $N \rightarrow I'$ transitions. However the differences in the vibrational patterns seem too great to enable the analogy to be made very rigid. There are two empirical arguments which apparently indicate that these bands correspond to the excitation of a ' π ' electron originally in the double bond. One is that such strong broad band systems do not occur in the spectra of molecules with single bonds (for example, chlorine monoxide). Secondly, Table III shows that as the heat of formation of the molecules from their atoms decrease (in accordance with the electronic formulæ, that is with decrease in number of bonding ' π ' electrons) so also does the frequency of the maximum. This would be expected for an $N \rightarrow I'$ transition.

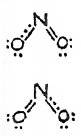
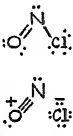
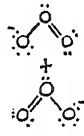
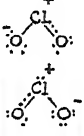
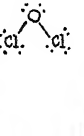
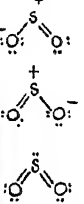
¹⁹ J. A. A. Ketelaar and K. J. Palmer, *J. Amer. Chem. Soc.*, 1937, **59**, 2629.

²⁰ C. F. Goodeve and S. Katz, *Proc. Roy. Soc., A.*, 1939, **172**, 432.

²¹ C. F. Goodeve and C. P. Stein, *Trans. Faraday Soc.*, 1929, **25**, 738.

Sulphur dioxide is an exception (H 255.4 Kcal., λ_{\max} , 1900 Å), probably because of the low ionization potential of sulphur. A rough correction for this might be made, by adding to the frequency observed the difference in the ionization potentials of the oxygen and sulphur atoms (in suitable units). This would make the band maximum at about 1200 Å,

TABLE III.

Molecule.	NO ₂ .	NOCl.	O ₃ .	ClO ₂ .	Cl ₂ O.	SO ₂ .
Heat of formation from atoms [H] in K. cal.	195.3	160.3	142.8	123.6	98.7	255.4
λ_{\max} . of strongest ultra-violet band	1450 Å 69000 cm. ⁻¹	1900 Å 52600 cm. ⁻¹	2550 Å 39200 cm. ⁻¹	3300 Å 30300 cm. ⁻¹	No comparable absorption	1900 Å 52600 cm. ⁻¹
Main contributing structures.						

which is approximately the wavelength at which it should appear in a molecule of first period atoms for which $H = 255.4$ Kcal. From this it would seem probable that in sulphur dioxide, as in the other molecules considered, the excitation giving rise to the 2300–1800 Å system is due to an electron originating in the π bond rather than to the transition of an electron from a non-bonding to an anti-bonding orbital.

Summary.

The absorption spectra of nitrogen dioxide, ozone and nitrosyl chloride have been investigated in the vacuum ultra-violet. They have been considered as examples of the class of triatomic molecules having more than sixteen outer electrons. It is concluded that certain band systems which have wide vibrational structure are probably due to the excitation of ' π ' bonding electrons.

Bands of a Rydberg type have been observed for nitrogen dioxide. These yield a value of 12.3 ± 0.2 v. for the ionization potential of the molecule. The electron ionized is a 2 p[O] electron, and the bond distances and the angle are not much affected in the process.

An attempt is made to correlate common features of the spectra, and to link them to the heats of formation of the molecules.

We are indebted to Dr. F. S. Dainton for preparing the specially pure samples of nitrogen dioxide and nitrosyl chloride, and to the Department of Scientific and Industrial Research (W. C. P.), and to the Goldsmiths Company (D. M. S.) for financial aid in connection with this work.

*The Laboratory of Physical Chemistry,
Cambridge.*

REVIEWS OF BOOKS.

Practical Microscopical Metallography. By R. H. GREAVES, D.Sc., and H. WRIGHTON, B.MET. Third Edition, Revised and Enlarged, 1939. Chapman & Hall Ltd., London. xi + 272 pp. 18s. net.

The Principles of Metallographic Practice. By GEORGE L. KEHL, M.S., 1939. McGraw-Hill Publishing Co. Ltd., London. xi + 239 pp. 21s. net.

ALTHOUGH these two books differ markedly in their scope, they have one important feature in common: they give the reader clear and precise instructions on how to use certain metallographical laboratory equipment. In the early days of metallography, it appears to have been thought in many quarters that a student acquired by instinct the capacity to use a microscope, much as a duck takes to water. Whether this was due to inertia on the part of those responsible for imparting metallographical knowledge or to their actual ignorance of the theory and use of the microscope is perhaps questionable, but one has only to look at some of the appalling "photomicrographs" which disfigure the pages of many serious papers on metallography published forty years or so ago to realise that even professors and lecturers in this subject appear to have been satisfied to use their microscopes under conditions which violated the fundamental principles of microscopic vision.

Conditions are very much better nowadays and for this improvement one must give credit to authors like Dr. Greaves and Mr. Wrighton who not only produce photomicrographs of the highest quality but also instruct their readers on how it is done.

The plan of the new edition of their book remains as in previous editions, the text having been revised and brought up to date. The authors' intention has been to provide, within a small compass, a set of typical photomicrographs suitably annotated and accompanied by a concise account of the results of metallographic researches and other investigations, in so far as they afford an interpretation of the structures observed in commercial materials. The photomicrographs are excellent and, we can well believe, are at once the envy and despair of many a student of metallurgical photomicrography. He should take heart however, and follow the authors' directions on how it is done!

Mr. Kehl's book is not a textbook on metallography as such but of the methods used in metallographic investigations. He describes in detail how to prepare samples for microscopic examination, how to etch them, how to use a microscope to examine them and how to record photographically what can be seen through the microscope. Methods of macroscopic observation and reproduction are next described and then hardness testing. Other chapters deal with pyrometry and thermal analysis and with special tests, *e.g.*, grain size measurements, magnetic tests, spark tests, cupping tests and the like.

One can congratulate the author on having accomplished in a successful manner what he set out to do, namely, "to bridge the gap between theoretical physical metallurgy and its practical application in the laboratory" and also express the hope that many metallurgical students will study what he has written.

J. H. G. M.

Sampling and Analysis of Carbon and Alloy Steels. Prepared by the Chemists Committee of the Subsidiary Companies of the United States Steel Corporation. (1938.) Reinhold Publishing Corporation, New York. Chapman & Hall Ltd., London. 356 pp. 22s. 6d. net.

Probably the first impression one has on perusing this book is the complexity which may be found in modern alloy steels. Before the days of the general use of alloy steels, an ordinary "complete" analysis of steel involved determinations of C, Si, Mn, S, and P. The book under review describes in detail the procedures to be adopted for determining the contents not only of these five elements but also of Cu, Cr, Ni, V, Mo, Ti, Al (and alumina), As, Co, W, U, Zr, Co, Ta, Se, B, N, Sb, Sn, and Zn, though of course not all of these are to be regarded as alloying metals producing beneficial results. Suggestions are also given for determining Be and Ce and the committee also discuss in some detail methods which have been proposed for the determination of O (or oxides) and H in steels, but they do not recommend any specific procedure for these particular gases as they consider no method of sufficient accuracy has yet been evolved.

It will be seen that the book is comprehensive, covering most of the demands likely to be made on a steel works chemist. One omission may be noted—Pb—which has come into some prominence in the United States recently (actually since the book was prepared), in the production of free machining steels. It may also be noted that spectrographic methods are not included, probably for a similar reason as suggested in the case of Pb; at the time the book was prepared, the use of the spectroscope as an accurate quantitative tool in the analysis of steel was in its infancy.

The preparation of the book has obviously been conducted with very great care, a fact not surprising, as the committee responsible for its production consists of more than a dozen chief chemists of laboratories engaged day in and day out in the analysis of steels of all types, from the cheapest and plainest carbon steel to such expensive and complex materials as corrosion-resisting and heat-resisting steels and high speed tool steels. They have considered, on the one hand, the extreme accuracy required in "referee" tests and, on the other hand, the need for rapid but nevertheless substantially accurate methods suitable for control purposes during the actual manufacture of steel. In both cases, the procedure recommended has been devised so as to eliminate as far as possible the "human element."

There can be no question that the efforts of the committee have resulted in the production of a book of the greatest value to steel works chemists. It should find a place on their bookshelves where it can readily be consulted.

J. H. G. M.

Chambers's Technical Dictionary. Edited by C. F. TWEENEY and J. E. C. HUGHES. (London and Edinburgh: W. & R. Chambers Ltd, 1940. Pp. vi + 957. Price 15s. net.)

This dictionary covers the definitions of terms used in astronomy, chemistry, physics, meteorology, mineralogy, geology, botany and zoology; in the medical and veterinary sciences; in psychology; in architecture; in engineering; and in the principal industries, including the printing and

bookbinding trades. It will be seen that the editors have embarked on an ambitious scheme, and a trustworthy estimate of their performance is far beyond the scope of any one reviewer.

But certain general principles can be laid down to which such a dictionary should conform. Definitions must be clear; full; unambiguous; precise; and as brief as the terms defined will allow. Moreover, even when, as with the dictionary under review, some forty thousand terms, more or less, are defined, it is impossible to include all the terms employed in the divisions of knowledge surveyed. A certain latitude of choice must be permitted to the editors; and the necessary and sufficient test of the wisdom of their choice is supplied by the answer to the question—how often does the dictionary fail the user?

The dictionary can be tested only by putting it into the hands of experts in some of the sciences surveyed. It has been tried by this method and has come triumphantly through the test. The definitions *are* clear, concise, accurate and up to date. Fundamental terms are defined, and out-of-the-way terms are not neglected—the dictionary, indeed, provides most fascinating and unexpected glimpses into the unknown to the reader who is not well-versed in any science or industry which comes within its scope.

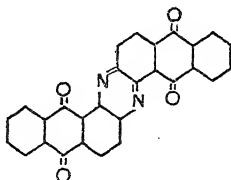
Here and there, swimming rare in the vast whirlpool, one or two inaccuracies may be detected by the pernickety critic; they are, however, very few, and serve but to throw up in stronger light the accuracy which is characteristic of the book. The definition of Helmholtz galvanometer is a case in point (" . . . two coils parallel to each other a few inches apart"). The galvanometer will not fulfil the Helmholtz condition unless the diameters of the coils are twice "a few inches." Again, Newton's law of cooling, for bodies cooling under the conditions laid down by Newton, holds for very large temperature excesses.

The book is clearly printed, well produced, and convenient to handle. It merits, and should be assured of, success.

A. F.

ERRATUM.

This vol., p. 69, Formula VIII should read



The Faraday Society

MINUTES OF A SPECIAL GENERAL MEETING

held on Thursday, 9th January, 1941, at 4 p.m. at the
Hotel Rembrandt, London, S.W. 7.

The Secretary read the Notice convening the meeting and explained that the object of the resolution was to give the Society power to retain the President, Officers and Council of the Society in office during the war.

On the motion of Dr. R. K. Schofield, seconded by Dr. A. King, it was resolved that a new Rule 20 as follows be adopted :—

“During the present war, those provisions of Rules 19 and 20 whereby the President, Vice-Presidents and ordinary Members of Council are not eligible to hold office for more than the periods in these Rules mentioned shall cease to have effect.”

This concluded the business of the meeting.

MINUTES OF THE THIRTY-FOURTH ANNUAL GENERAL MEETING

held on Thursday, 9th January, 1941, at 4.5 p.m. at the
Hotel Rembrandt, London, S.W. 7.

1. The Minutes of the Thirty-third Annual General Meeting were taken as read and confirmed.

2. The Secretary conveyed the regrets of the Honorary Treasurer that urgent national duties precluded his presence at the meeting, and on his behalf submitted the Annual Report and Statement of Accounts for the year 1939. The President said that the Society was greatly indebted to Dr. Slade for his services as Honorary Treasurer in these difficult times; the fact that this Society was not in the financial

difficulties which faced some other societies was largely due to the care which Dr. Slade had taken over the Society's financial affairs.

In moving the adoption of the Annual Report and the Statement of Accounts, the Secretary said that a perusal of the Report and the Accounts showed that the Society's finances were in sound condition. The year under review (1939) included the receipt of subscriptions from members resident in countries in enemy occupation; such revenue was of course not to be looked for again until that occupation ceased. The adoption having been proposed by Professor C. H. Desch and seconded by Professor H. J. Emeléus, the Report and Statement of Accounts were duly adopted.

3. Dr. R. K. Schofield proposed, and Prof. H. J. Emeléus seconded the resolution that the President, Officers and Council be re-elected for the year 1940/41 in accordance with the Rule just adopted, and the President declared the Council to be so re-elected as follows :—

President.

PROF. E. K. RIDEAL, M.B.E., D.Sc., F.R.S.

Vice-Presidents who have held the Office of President.

SIR ROBERT ROBERTSON, K.B.E., D.Sc., F.R.S.

PROF. F. G. DONNAN, C.B.E., Ph.D., F.R.S.

PROF. C. H. DESCH, D.Sc., F.R.S.

PROF. N. V. SIDGWICK, Sc.D., D.Sc., F.R.S.

PROF. M. W. TRAVERS, D.Sc., F.R.S.

Vice-Presidents.

PROF. J. E. COATES, O.B.E., D.Sc. PROF. W. C. M. LEWIS, D.Sc., M.A., F.R.S.

PROF. A. FERGUSON, D.Sc. C. C. PATERSON, O.B.E.

PROF. R. H. FOWLER, O.B.E., PROF. R. WHYTLOW-GRAY, O.B.E.,
M.A., F.R.S. Ph.D., F.R.S.

Honorary Treasurer.

R. E. SLADE, D.Sc.

Chairman of the Publications Committee.

PROF. A. J. ALLMAND, D.Sc., F.R.S.

Council.

E. J. BOWEN, M.A., F.R.S.

F. D. MILES, D.Sc.

C. R. BURY, B.A.

W. J. SHUTT, D.Sc.

J. J. FOX, O.B.E., D.Sc.

D. W. G. STYLE, Ph.D.

PROF. W. E. GARNER, D.Sc., F.R.S.

PROF. S. SUGDEN, D.Sc., F.R.S.

R. LESSING, Ph.D.

O. J. WALKER, Ph.D.

This concluded the business of the meeting.

INTERFACIAL TENSION, VISCOSITY AND POTENTIAL CHANGES PRODUCED BY INSOLUBLE MONOLAYERS AT THE OIL/WATER INTERFACE.

BY A. E. ALEXANDER.

Received 11th December, 1940.

Methods for determining the above quantities, generally denoted by F , η and ΔV respectively, as a function of the area per molecule (A), are well standardised for monolayers at the air/water (A/W) interface,^{1, 2} but numerous difficulties appear when an extension to the oil/water (O/W) interface is attempted. Recently, however, considerable progress has been made, and these can now be determined with an accuracy which, in the case of the interfacial tensions (I.T.s) at any rate, approaches that at the A/W interface.

Experimental Methods at the O/W Interface.

(a) **Interfacial Tension Changes.**—A directly modified Langmuir-Adam balance was used for the first attempts,^{3, 4} but as the authors point out, very great difficulties due to leaks and contamination are encountered. A very much better method⁵ is to determine the I.T. by means of the ring method and, keeping the total area constant, to decrease the area per molecule by successive injections of the spreading material. This overcomes troubles due to leaks and changing interfacial contact angle, and adequate cleaning of the interface can be readily obtained if oils lighter than water are used. It is of interest to note that this method gives excellent results at the A/W interface also.

(b) **Interfacial Viscosity Changes.**—A few preliminary measurements⁶ have shown that, using a platinum needle for the oscillating vane, the oscillation method developed by Fourt and Harkins^{7, 8} can be employed provided a sufficiently thin film (about 2 to 3 mm.) of the lighter phase is used. The area per molecule is varied as above.

(c) **Interfacial Potential Changes.**—The usual methods which have been employed for studying phase boundary potentials at the O/W interface⁹ become useless with pure hydrocarbon oils on account of the very high resistance introduced. However, by using a very thin

¹ For a review of F and ΔV measurements see Adam, *The Physics and Chemistry of Surfaces*, 2nd edit., 1938, O.U. Press.

² For a review of η measurements see Schulman, *Ann. Reports Chem. Soc.*, 1939, p. 94.

³ Askew and Danielli, *Proc. Roy. Soc. A*, 1936, **155**, 695.

⁴ Askew and Danielli, *Trans. Faraday Soc.*, 1940, **36**, 785.

⁵ Alexander and Teorell, *ibid.*, 1939, **35**, 727.

⁶ Carried out by Mr. Crisp in this laboratory at the request of the author.

⁷ Fourt and Harkins, *J. Physical Chem.*, 1938, **42**, 897.

⁸ Fourt, *ibid.*, 1939, **43**, 887.

⁹ Dean, *Trans. Faraday Soc.*, 1940, **36**, 166.

film (about 1 to 2 mm.) of the oil phase spread on the water surface, and a very large (4 cm.²) polonium electrode to decrease the air-gap resistance,⁵ measurements can be obtained by the method used at the A/W interface. A Lindemann electrometer can be used, but better results are obtained with a valve electrometer having a very stable zero. (The circuit described by Henney²² which employs the G.E.C. FP54 Valve was found to be excellent.)

The molecular area is varied by the usual spreading technique.

Comparison of Results at O/W and A/W Interfaces.

(a) Interfacial Tension Changes.

A comparison between the force-area curves^{4, 5} given by the same compound at both interfaces shows at once the enormous expansion brought about by the oil phase, as might have been anticipated. Coherent liquid films at the A/W interface, such as are given by the proteins, lecithin, etc., pass over into gaseous or vapour expanded films at the O/W. Myers and Harkins^{11, 12} also found that addition of hydrocarbon oils caused a large expansion of the liquid-expanded films of oleic and myristic acids, but had little effect on the condensed film of stearic acid.

On compression, it can be seen from Table I that the areas of a given

TABLE I.

SMALLEST AREAS OBSERVED (FOR STABLE FILMS).

Compound.	A/W Interface.	O/W Interface.
Lecithin . . .	ca. 73 Å ² 20	ca. 75 Å ² 5
Kephalin . . .	ca. 60 Å ² 23	ca. 60 Å ² 10
Lyssolecithin . . .	ca. 66 Å ² 20	ca. 60 Å ² 5
Sodium cetyl sulphate . . .	—	ca. 35 Å ² 5
α-Amino-palmitic acid . . .	—	ca. 28 Å ² 4
α-Amino-stearic acid . . .	ca. 25 Å ² 21	—
Serum albumin (20 dynes)	0.4 m. ² /mg. ⁵	0.4 m. ² /mg. ⁵

(Oil phase, bromobenzene for α-amino-palmitic acid, benzene for the remainder.)

compound at the two interfaces approach one another and eventually, if the monolayers are sufficiently stable, an identical packing seems to be obtained. No discontinuities on compression at the O/W interface have yet been observed, and the physical state of the close-packed interfacial film seems to be the

same in both cases (*e.g.* gelation of proteins,⁵ solidification of α-amino-palmitic acid⁴ and heptadecylamine sulphate.¹⁸ These results indicate very strongly that with stable monolayers the oil phase is eventually squeezed out completely; with benzene when *F* exceeds about 20 dynes. Myers and Harkins,^{11, 12} have also shown that compression to about 15 dynes of a mixed monolayer of fatty acid and long-chain hydrocarbon causes the latter to be more or less completely eliminated as small lenses. This squeezing out of the oil phase is extremely important, since it shows that a similar behaviour is to be expected at both interfaces provided the lowerings of the I.T. are reasonably great (*e.g.* more than about 20 dynes), and, of course, that any solubility in the oil phase is allowed for. Accordingly, in such cases, a

¹⁰ Alexander, Teorell and Åborg, *Trans. Faraday Soc.*, 1939, **35**, 1200.

¹¹ Myers and Harkins, *J. Physical Chem.*, 1936, **40**, 959.

¹² Harkins and Myers, *J.A.C.S.*, 1936, **58**, 1817; 1937, **59**, 593.

direct prediction of the behaviour at the O/W interface can be obtained from the much more readily performed experiments at the A/W interface. For smaller lowerings of the I.T., or for O/W interfaces having an initial value much less than 20 dynes, such correlation is no longer possible.

Equation of State.—At the O/W interface all the simple compounds examined by Teorell and the author^{5, 10} give $F-A$ curves which fit the hyperbolic equation $(F-F_0)(A-A_0) = C$, where F_0 , A_0 , and C are constants. The values of these constants are shown in Table II, which also includes the values for the A/W interface if a similar equation of state is obeyed there.

TABLE II.

Compound.	Benzene/Water.			Air/Water.		
	$-F_0$ (dynes).	A_0 (Å ²).	C	$-F_0$ (dynes)	A_0 (Å ²).	C
Lysolecithin . . .	0.05	40.4	575	12.8	42.8	686
Lecithin . . .	0.36	58	737	8.7	51.2	728
Kephalin . . .	0.7	49.5	593	Very similar to	lecithin.	
Sodium cetyl sulphate	0.15	13.9	729	—	—	—

The liquid expanded films at the A/W interface have been explained by Langmuir¹³ on the basis of cohesive forces between the long chains, finite areas occupied by the head-groups, and two-dimensional thermal agitation of the heads, giving the $-F_0$, A_0 and C terms respectively. Accordingly, at the O/W interface F_0 should be practically eliminated, whereas A_0 and C should be unaltered. So far as the data permit, this appears from Table II to be confirmed.

"Surface Ageing."—Very dilute solutions of many compounds, particularly long-chain colloidal electrolytes, are well known to take abnormally long times (of the order 10^6 that predicted from classical diffusion theory) before the surface tension reaches its equilibrium value. At the O/W interface this time lag is eliminated, even when the oil phase is reduced to monolayer thickness by the use of piston oils such as oleic acid and ethyl laurate.¹⁴ Earlier theories, based either upon an electrostatic repulsive barrier at the surface,¹⁵ or upon formation of polymolecular leaflets,¹⁶ are quite inadequate to explain these and other facts and the explanation now suggested¹⁴ ascribes the time factor to a slow penetration and reorientation of the hydrocarbon portion of the molecule in the adsorbed surface film. The freely mobile hydrocarbon molecules at the O/W interface would greatly assist such changes and so remove the anomaly.

¹³ Langmuir, *J. Chem. Physics*, 1933, **1**, 756.

¹⁴ Alexander, *Trans. Faraday Soc.*, 1941, **37**, 15.

¹⁵ Doss, *Kolloid Z.*, 1938, **84**, 138; 1939, **86**, 205.

¹⁶ McBain and Perry, *J. Ind. and Eng. Chem.*, 1939, **31**, 35.

¹⁷ Schulman and Cockbain, *Trans. Faraday Soc.*, 1940, **36**, 662.

¹⁸ Alexander and Schulman, *ibid.*, 960.

¹⁹ Dean, Gatty and Rideal, *ibid.*, 161, 166, 173.

²⁰ Hughes, *Biochem. J.*, 1935, **29**, 430.

²¹ Porter, *J.A.C.S.*, 1937, **59**, 1883.

²² Henney, *Electron Tubes in Industry*, McGraw-Hill, 1937, p. 91.

²³ Teorell, unpublished results.

²⁴ Alexander and Teorell, unpublished results.

Complex Formation.—Experiments upon mixed monolayers at the A/W interface²⁵ have shown that in some cases, *e.g.*, cholesterol and sodium cetyl sulphate, the resultant surface tension is very much lower than that given by either component separately. Such effects have been ascribed to "complex" formation. Using emulsion systems, recent experiments indicated that complex formation existed at the O/W interface also.²⁶ This has recently been confirmed by direct I.T. measurements upon the benzene/water system, which showed that complexes are definitely formed at this interface and that their stability runs parallel to that at the A/W interface.²⁷ A close resemblance between the physical nature of the interfacial films at the two interfaces was also noticed.

(b) Interfacial Viscosity Changes.

At the A/W interface introduction of bi- or poly-valent anions beneath a gaseous monolayer of a long-chain amine hydrochloride is known to bring about solidification of the film.¹⁷ A similar reaction occurs at the O/W interface¹⁸ and can conveniently be followed by the change in interfacial viscosity.⁶

The transition of protein monolayers at the O/W interface from the fluid to the gel state can be studied similarly.

(c) Interfacial Potential Changes.

Dean⁹ records observations on the changes in interfacial potential brought about by spreading albumen monolayers and the effect of tannic acid on these, which were in qualitative agreement with results at the A/W interface. No measurement of the areas involved was, however, attempted. Myers and Harkins^{11,12} have published one ΔV - A curve for a mixture of pentadecylic acid and nujol which agrees very approximately with that of the acid alone.

Teorell and the author²⁴ have carried out a number of measurements at the benzene/water interface, using lecithin as the spreading material since this gives the most stable films of any compound so far examined. The plot of ΔV against the molecular concentration n (molecules/cm.²) is linear from the largest areas studied (about 1000A²) down to about 100A², when it commences to bend towards the n axis. The linear portion gives, from the Helmholtz equation $\Delta V = 4\pi n\mu$, a value for μ in fair agreement with that found at the limiting area at the A/W interface²⁰ (about 880 milli-Debyes). This result, although of a preliminary nature, is of much interest, as it indicates freely moving molecules with very small lateral cohesion as suggested by the above equation of state, and a similar dipole orientation and value of μ at both the A/W and O/W interfaces.

These interfacial potential changes at the benzene/water interface were moderately reproducible and showed no decrease with time. Addition of nitrobenzene to decrease the resistance of the oil phase caused the potential change to decrease on standing, the rate increasing with the concentration of nitrobenzene. These results are in agreement with those of Dean,⁹ using various oils and albumen monolayers. The reasons

²⁵ Schulman and Rideal, *Proc. Roy. Soc. B*, 1937, **122**, 29; Schulman and Stenhagen, *ibid.*, 1938, **126**, 356.

²⁶ Schulman and Cockbain, *Trans. Faraday Soc.*, 1940, **36**, 651, 661.

²⁷ Alexander and Schulman, *ibid.*, 960.

for obtaining a stable, reproducible change in phase boundary potential at the A/W interface have recently been put forward by Dean, Gatty and Rideal.¹⁹ Similar considerations would apply when using an oil, such as benzene, which has an extremely high resistance.

Summary.

A brief survey is given of the possible methods of measuring changes in the interfacial tension, viscosity and potential brought about by spreading insoluble monolayers at the O/W interface.

The results of such measurements are compared with those obtained with the same or related compounds at the A/W interface. For small values of F (i.e. small lowerings of the I.T.), the areas at the O/W interface are very much greater than at the A/W, but as F increases the two approach until an identical packing is obtained. From the equation of state and the changes in interfacial potential it appears that very considerable information can be obtained about the properties of monolayers at the O/W interface from measurements at the A/W.

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CELL PERMEABILITY AND DIFFUSION ACROSS THE OIL-WATER INTERFACE.

BY JAMES FREDERIC DANIELLI.*

Received 6th December, 1940.

The cell plasma membrane is, to a first approximation, a thin layer of lipid (sterols, phosphatides and fats), not more than 10^{-6} cm. in thickness, stabilised by adsorbed protein layers at the two oil-water interfaces.¹ The problem of diffusion across this layer of predominantly hydrocarbon material is one of the fundamental problems of biology.

Such a membrane presents resistances to the free diffusion of three types: (a) at the membrane interface, diffusion from water \rightarrow oil; (b) at the membrane interface, diffusion oil \rightarrow water; (c) in the interior of the membrane. For molecules of the type $R(OH)_x$, where R is hydrocarbon in character, resistance (a) is mainly due to the necessity of breaking hydrogen bonds between the OH groups and water; ² resistance (b), where large, is mainly due to the difficulty of moving the hydrocarbon residue R from the oil layer into the aqueous phase; resistance (c) is similar to that met in diffusion through a paraffin oil of viscosity perhaps 10^5 times that of water. Where $x > 2$, the resistance to diffusion across the interface in the direction water \rightarrow oil is, for most cells, so much larger than the other resistances as to become the controlling factor.

To obtain equations for the rate of penetration, assumptions must be made about the mechanism of diffusion. I have tried two sets of assumptions: (1) the interfacial resistances (a) and (b) may be replaced by single potential energy jumps, μ_a and μ_b , and Fick's equation applies to

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¹ See *Review*, Harvey and Danielli, 1938; *Biol. Rev.*, 13, 319.

² As was suggested to me by Professor J. D. Bernal.

diffusion in the interior of the membrane; (2) the interfacial resistances again are replaced by single potential energy jumps and the interior of the membrane is regarded as a succession of potential energy maxima and minima, involving a jump of height μ_e . Then with both sets of assumptions we have for diffusion from water to oil:

$$dN/dt = aC \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and from oil to water:

$$dN'/dt = bC' \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where C and C' are the concentrations in the water layer and oil layer respectively. In addition, in the interior of the membrane with assumptions (1) we have:

$$\frac{\partial S}{\partial t} = -D \frac{\partial C}{\partial x} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and with assumptions (2), for diffusion across the r th potential energy maximum:

$$dN_r/dt = \epsilon C_r \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where C_r = concentration in the r th minimum. a , b , ϵ , and D are constants at constant temperature. If there are n maxima in the membrane thickness,

$$D = \frac{n+1}{n} \lambda \epsilon,$$

where λ = distance between potential energy maxima.

Let the permeability P of the membrane be defined by (5):

$$dS/dt = P(C - C_1), \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where C_1 is the concentration inside the cell. C_1 is assumed to be constant throughout the cell. All the quantities refer to 1 cm.² of membrane. Then, with assumptions (1) we find that within the range of values of a , b and D , possible in cases where permeation can be observed, no appreciable concentration variation develops in the membrane itself at any one time, provided diffusion through the membrane is much slower than diffusion through the two aqueous phases, and $\frac{bl_2}{D}$ is small compared with 1; l_2 = thickness of the membrane (ca. 10^{-6} cm.).

Then:

$$\frac{C_1 - C}{C} = \frac{m_2}{m_1 - m_2} e^{m_1 t} - \frac{m_1}{m_1 - m_2} e^{m_2 t} \quad . \quad . \quad . \quad . \quad . \quad (6)^{\frac{2}{3}}$$

where

$$m_1 = \frac{b}{l_2} \left[-\frac{al_2}{2bl_3} + \frac{1}{2} \left(\frac{al_2}{2bl_3} \right)^2 \cdot \cdot \cdot \right]$$

$$m_2 = \frac{b}{l_2} \left[-2 - \frac{al_2}{2bl_3} - \frac{1}{2} \left(\frac{al_2}{2bl_3} \right)^2 \cdot \cdot \cdot \right]$$

l_3 = "equivalent thickness" of cell, i.e. volume per cm.² of membrane ≤ 1 .

³ I am greatly indebted to Mr. F. J. Turton for these two results. Neither result is correct during the initial period in which the concentration ratio across the interface is falling from ∞ to a finite value.

water.⁶ These values are given in Table I, together with values for typical cells.⁷ The calculated values are of the same magnitude as the experimental values for both oils, except in the case of glycol penetrating olive oil, where the permeability is too high. An effective model of the cell membrane requires a viscosity about 10^5 times that of water.

TABLE I.

COMPARISON OF PERMEABILITY OF THIN OIL LAYERS CALCULATED FROM EQUATIONS (8) AND (11) WITH EXPERIMENTAL VALUES OF THE PERMEABILITY OF CELLS. PERMEABILITY IN MOL./SEC./ μ^2 PER MOL. PER LITRE CONCENTRATION DIFFERENCE, $\times 10^{16}$.

	5 $m\mu$ olive oil, $\eta = 1$ poise.	5 $m\mu$ oil, $\eta = 10^4$ poise.	Ox erythro- cyte.	<i>Arbacia</i> egg.	<i>Chara</i> <i>ceratophylla</i> .	<i>Plagio-</i> <i>thecum</i> <i>denticu-</i> <i>latum</i> .	<i>Pylaiella</i> <i>litoralis</i> .
Ethylene glycol .	100	0.01	0.2	0.73	1.2	0.03	0.1
Glycerol .	0.002	0.002	0.002	0.005	0.02	0.0003	0.002
Erythritol .	0.00005	0.00005	—	—	0.001	0.00007	0.0001

The Relationship between Permeability and Partition Coefficients.

Case (1): substituting from (11) in (9) we obtain:

$$PM^{\frac{1}{2}} = a/b \times \text{constant at constant temperature} \quad (12)^8$$

Case (2): dividing both sides of (7) by b and substituting from (11) we obtain:

$$PM^{\frac{1}{2}} e^{\frac{\mu_b}{RT}} = a/b \times \text{constant at constant temperature} \quad (13)^8$$

These relationships (12) and (13) are linear relationships between $PM^{\frac{1}{2}}$ in the one case and $PM^{\frac{1}{2}} e^{\frac{\mu_b}{RT}}$ in the other case, and the partition coefficient a/b . These relationships are obeyed approximately by the experimental results for all cells for which sufficient data are available (about 15 different cells).

Further progress in our ability to analyse results in the field of cell permeability is dependent on replacing equation (11) by a more satisfactory relationship.

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⁶ $r\phi$ has been taken as 10^6 , the value obtained from diffusion constants in oils, assuming $\lambda = 10^{-6}$ cm.

⁷ The experimental values are from Collander and Bärlund, 1933: *Acta Bot. Fennica*, 11, 1; Marklund, 1936: *ibid.*, 18, 1; Jacobs and Stewart, 1932: *J. Cell. Comp. Physiol.*, 1, 71.

⁸ Assuming that $r\phi$ has the same value for all molecular species.

THE STRUCTURE AND PROPERTIES OF FAT PARTICLES IN HUMAN SERUM.

By A. C. FRAZER.*

Received 24th December, 1940.

Bright particles in violent Brownian movement can be seen in normal plasma or serum examined under dark-ground illumination. Differing views have been held as to the composition of these particles. The object of this paper is to put forward the evidence upon which it is concluded that these particles are fat, the investigations indicating the probable structure at the oil/water interface, and certain experiments which suggest the possible importance of this interface in biological phenomena.

The Structure of the Particles.

Biochemical Investigations.

If samples of blood are analysed to determine their neutral fat, phospholipid, cholesterol and protein content, and these results are compared with counts of the particles made on the same blood samples, the only factor showing parallel changes with the particle counts is the neutral fat. The different protein fractions were also studied, but changes were found to be quite unrelated to the particle counts.

After centrifugation at various speeds the particles are always most numerous in the upper layers, and again correlation with neutral fat can be demonstrated by analysis.

Physiological Investigations.

The number of particles in the blood varies under differing physiological conditions. There is a marked rise in the number after ingestion of food, and in starvation sudden increases occur at regular intervals, starting on the third day. The former, exogenous, increase only follows the ingestion of fat, and is never seen after a meal of carbohydrate or protein alone. In hundreds of particle counts this close relationship between the intake of fat and the number of particles in the blood has always been found. The endogenous increase of particles which is seen in starvation coincides with the onset of ketosis which is indicative of an augmented fat utilisation. The injection of fat-mobilising hormones, ether anaesthesia, repeated haemorrhage and other conditions known to give rise to an increase in blood fat, all furnish an identical blood picture with a marked increase in the number of bright particles.

These physiological and biochemical studies are more fully described elsewhere,^{1, 2} but it is apparent that neutral fat is the only blood constituent that shows quantitative variations parallel with the number of bright particles.

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¹ A. C. Frazer and H. C. Stewart, *J. Physiol.*, 1937, 90, 18.

² J. J. Elkes, A. C. Frazer, and H. C. Stewart, *ibid.*, 1939, 95, 68.

The Oil/Water Interface.

Assuming that these particles are fat, a study of their behaviour to change of environment in the continuous phase throws some light on the structure at the oil/water interface.

Action of Fat Solvents.—Attempts to dissolve the particles, without gross interference with the dark-ground picture, have failed. The fat solvents can be considered in three groups. One group, including alcohol and acetone, caused a striking increase in the number of particles in the dark-ground field, presumably due to the precipitation of protein. Benzene and toluene are in the second group, and undergo spontaneous emulsification in the plasma filling the field with a teeming mass of brightly illuminated particles. The third, containing petroleum ether and xylene, appears to have no effect at all.

Precipitation Reactions.—The behaviour of the particles with precipitants strongly suggests their close association with protein. Half-saturation with ammonium sulphate causes the particles to aggregate in feathery clumps. A similar picture is seen with full saturation with sodium chloride. There is no apparent increase in the number of particles in the field in either of these reactions. Full saturation with ammonium sulphate results in a marked increase in the number of particles and the formation of large immobile clumps rapidly occurs. Similar changes are seen with the addition of other protein precipitants.

Electrophoresis.—Dark-ground electrophoretic study of the particles was made in a special cell, consisting of a thin film of serum enclosed by a coverslip on a microscope slide, and overlapping the electrodes which were formed from gold leaf transfers at each end of the slide. The particles were found to carry a negative charge. This was confirmed by experiments in larger electrophoretic chambers, but it was found impossible to separate the fat and protein components of plasma by this means.

Effect of pH .—The reaction of the plasma was varied by the addition of acid, and the behaviour of the particles in a pH range from 7.4 to 1 was examined. The pH of the mixtures was checked by estimation with the glass electrode method.

No change is seen in the particles as the pH is varied from 7.4 to 6.0. At this point small feathery clumps appear and at pH 5.3 complete immobility of the particles occurs. Below pH 5.0 normal distribution and mobility of the particles is again evident, and between pH 2 and 1 there is a sudden great increase in the number of particles and massive groups of stationary particles accumulate in the field.

Protection of Soap-stabilised Oil-in-water Emulsion by Protein.³—Approaching the problem from a different angle, it was found that a finely dispersed 5 % olive oil in water emulsion stabilised with 0.2 % of sodium oleate with an average particle size of less than 0.5μ exhibited creaming if mixed with 0.9 % NaCl solution. The addition of a small amount of protein to the emulsion prior to the addition of the saline afforded complete protection against the creaming action of the latter. Thus, equal parts of 0.9 % NaCl and 5 % emulsion were left at room temperature for one hour, marked creaming was evident. A similar mixture using protein-protected emulsion showed no creaming in 3 days, and similar stability was demonstrable even in mixtures consisting of 9 parts of saline to 1 part of emulsion.

Protection is not only afforded against saline, but also against acid. Normally a soap stabilised emulsion breaks out completely at pH 6.0, but it will withstand a pH of 2 if protected with protein. Both albumin and globulin fractions, used separately, will protect the emulsions, but there is

³ A. C. Frazer and H. C. Stewart, *J. Physiol. P.*, 1939, 95, 5, 7.

evidence that in a mixture of albumin and globulin the latter is preferentially selected.

Behaviour of Protein-protected Fat Particles on Change of Environment.—If a finely dispersed oil-in-water emulsion protected with protein is treated with fat solvents, it is not possible to bring the fat into solution. Precipitation reactions of the particles are characteristic of the particular protein used for protection. Electrophoresis shows that the particles are negatively charged. The effect of change of reaction is indicated in Table I, where it will be seen that globulin appears to be associated with the fat particles in preference to albumin, if a mixture of the two is added to the emulsion. This is also borne out by the precipitation reactions.

TABLE I.

$p_{H.}$	Blood Particles.	Soap-stabilised O/W Emulsion.	Protein Protected Emulsion.	Albumin Protected.
8.0	N	N	N	N
7.0	N	N	N	N
6.0	N	C+	N	N
5.5	G	C++	G	N
5.0	G	C+++	G	N
4.5	N	C+++	N	G
4.0	N	C+++	N	G
3.0	N	C+++	N	N
2.0	P	C+++	P	P

N—normal movement and distribution.
 C—creaming.
 G—clumping and immobility.
 P—precipitation.

In all respects fat particles protected with a protein film behave identically with the particles described in normal human blood.

Biological Significance of the Oil/Water Interface.

Effect on Insulin Response.⁴—Injection of insulin into an animal normally causes a marked fall in the sugar content of the blood. If insulin is mixed prior to injection with a finely dispersed oil-in-water emulsion it no longer produces this response. This action of emulsion can be shown to be due to the particulate nature of the oil phase and cannot be attributed to any of the other constituents of the emulsion. In an animal with a low blood sugar due to an injection of insulin, intravenous administration of a finely dispersed oil emulsion results in an immediate rise in the sugar level. Finally, if the blood fat is increased in an animal by feeding, or by ether anaesthesia, injections of insulin fail to produce the normal response. The presence of fine particles of fat in the blood is thus closely associated with a condition of insulin resistance.

Effect on Agglutinins.—Agglutinins are one type of antibody which appear in the blood in certain diseases, and are closely related to the globulin fraction of the plasma protein; α and β agglutinin is found in normal plasma and its distribution determines the blood group. A rise in the blood fat is coincident with a fall in the titre of agglutinins. In a human subject with glandular fever, the ingestion of fat caused a fall in agglutinin titre of 50 %. The titre curve showed an exact correlation with the alterations in blood fat, the height of the titre being inversely proportional

⁴ H. C. Stewart, 1940 (*Personal communication*).

to the number of particles in the blood. Similar results were obtained with the α and β agglutinins of normal blood. Artificial oil-in-water emulsions had the same effect on the agglutinin titre, and control experiments with broken emulsion show the importance of the oil/water interface in this phenomenon.

Effect on Bacterial Toxins and Cobra Venom.^{5, 6, 7}—If a lethal dose of diphtheria or tetanus toxin is added to a finely dispersed emulsion prior to injection, it is rendered completely innocuous. Any of the constituents of the emulsion or coarsely dispersed emulsions of similar composition fail to detoxicate the toxins. Striking modification of the action of many other toxins when mixed with emulsions has also been observed. Cobra venom in a dose sufficient to kill in less than one hour is quite harmless if mixed with emulsion and administered intravenously. If the venom-emulsion mixture is given into the peritoneum, the animal dies. This has been shown to be due to the creaming of the emulsion with consequent liberation of the venom. Creaming does not occur in the blood stream because the plasma protein protects the emulsion from the effects of the body salts. Intravenous injection of emulsions in toxæmia causes a striking alleviation of the toxæmic symptoms. The mechanism of detoxication in all these experiments appears to be adsorption of the toxin at the oil/water interface.

Discussion.

The biochemical and physiological evidence strongly supports the view that the particles seen in the blood under dark-ground illumination are essentially neutral fat. Their behaviour with fat solvents, precipitants, and change of reaction suggests a very close association with protein, especially with the globulin fraction. The addition of protein to finely dispersed oil-in-water emulsion affords protection for the emulsion against salts and acid. This protection is probably due to the formation of a tough film of protein on the surface of the fat particle. The fat particles are also found to select the globulin from a mixture of albumin and globulin, so that a particle of fat added to the blood will be invested with a globulin film. If these protected emulsions are subjected to the same investigations as those carried out on the blood particles, no differences of behaviour can be detected between the two. The protected emulsions contain particles which are essentially neutral fat, but their reaction to their environment depends upon the presence of a globulin film at the oil/water interface. It is concluded that the particles in the blood seen under dark ground have this same structure.

The protein film is undoubtedly of importance in the maintenance of stability of the fat emulsion in the blood, but the oil/water interface has other fundamentally important biological functions. It is impossible at present to make any comprehensive survey of these functions but three groups of observations have been cited which serve to indicate some of the possibilities.

With the presence of an oil/water interface, globulin molecules will be orientated and further orientated layers of molecules may lie outside the primary film. This orientation may involve very considerable modification of the biological activity of the molecules concerned. That

⁵ A. C. Frazer and V. G. Walsh, *Brit. Med. J.*, 1934, i, 424.

⁶ A. C. Frazer and V. G. Walsh, *J. Pharm. Exp. Ther.*, 1939, 67, 476.

⁷ A. C. Frazer and H. C. Stewart, *Brit. J. Exp. Path.*, 1940, 21, 361.

this is the case is strongly suggested by the drop in agglutinin titre in blood containing particulate fat. Whether the agglutinins are a part of the primary globulin film or whether they are secondarily involved is not known. The production of a state of resistance to insulin action by the introduction of fat particles into the blood stream again demonstrates the profound effect of the oil/water interface. It seems probable that other hormones of a protein nature will undergo similar modification in the presence of blood fat. These observations at present suggest that hormones derived from other animals are inactivated by the fat, whereas the normal secretion put out by the animal's own glands are not affected. Further investigation is required to establish this point.

The experiments on toxins and cobra venom illustrate the possible effect of the oil/water interface on these lethal substances. There is unquestionable evidence of the presence of such an interface in the blood stream under various physiological conditions. Studies *in vitro* show a peculiar type of specificity in the adsorption of toxins, for when two different toxins are added to emulsion serially, the first toxin added is adsorbed, to the exclusion of the second. Whether such specific reactions occur *in vivo* has yet to be demonstrated. Until the precise physiological control of endogenous lipaemia has been elucidated, it is impossible to say to what extent the body makes use of the oil/water interface in the plasma as a protective mechanism against bacterial toxins, but there can be no doubt that such a weapon would constitute a most effective defence.

It is concluded that fat particles in the blood stream have a primary film of globulin at the oil/water interface which gives great stability to the emulsion. Orientation of protein molecules occurs at this interface which may greatly modify their effects on the body cells. This modification may be seen in normal constituents such as the agglutinins, or may be demonstrated by injection of hormones such as insulin. There is some evidence that it particularly affects protein substances which are foreign to the animal. It is suggested that this oil/water interface may be of importance as a protection against the effects of bacterial toxins. Further investigations may unfold the exact relationships and importance of these observations in the field of immunology.

Note :—

1. The term "creaming" is used throughout this paper to mean coalescence of fat globules. "Breaking" implies liberation of free oil.
2. Full references to original papers on the subjects discussed are given in the papers quoted and are not repeated here.

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INTERFACIAL ACTIVITY OF BRANCHED-PARAFFIN-CHAIN SALTS.

BY G. S. HARTLEY.

Received 27th December, 1940.

Any amphipathic¹ substance, *i.e.* one in which there is an asymmetrical distribution of water-attracting and indifferent groups in the molecule, will lower the interfacial tension (I.T.) between water and a non-polar liquid. It will do so by tending to accumulate in the interface, the water retaining the attracting group and expelling the indifferent one into the oil phase. The straight paraffin-chain salts have hitherto been the most generally effective simple compounds for lowering I.T. In these, the most water-attracting of all groups—an ionised one—is attached to the most indifferent of all—a saturated straight hydrocarbon chain.

If a close-packed monolayer of paraffin-chain ions could be built up in the interface, one might expect to find the I.T. falling to extremely low or even negative values. The latter would, of course, mean that true spontaneous emulsification would occur until the interfacial layers had been sufficiently diluted for a positive I.T. to be regained. In practice, I.T.'s of non-polar oils against water are not permanently reduced by simple paraffin-chain salts, already existing as such in either phase, below about 1 or 2 dynes/cm.,^{2, 3} and spontaneous emulsification does not occur in such systems.

I.T.-concentration curves in such systems show^{2, 3} that the initial steep fall of I.T. is arrested at the concentration which is known to be critical for the formation of micelles of the type characteristic of these salts.^{1, 4} That it should be so is quite to be expected, since the micelle itself is symmetrically hydrophilic: only the single ions are surface active.⁵ Otherwise considered, at this concentration another means becomes available to the water of expelling the intruding paraffin-chains *alternative* to that of pushing them into a pre-existing interface. Micelle formation is a parallel property to I.T. reduction, and, far from being the cause of it, as is sometimes suggested, it is in fact competitive.

If we could preserve the amphipathic property of the ion and inhibit micelle formation, we might therefore expect to secure greater lowering of I.T. We know that these micelles are essentially liquid with regard to their paraffin content, and are as large as possible consistent with this and with the ionised groups remaining in their surface.^{4, 6} That they are as large as possible indicates that they still allow some contact of paraffin and water.⁷ Clearly, if they had to be smaller they would leave more, would therefore provide a less satisfactory means for the

¹ Hartley, *Aqueous Solutions of Paraffin-chain Salts* [Hermann, Paris, 1936].

² Robinson, article in *Wetting and Detergency*, [Harvey, London, 1937].

³ Powney and Addison, *Trans. Faraday Soc.*, 1937, **33**, 1243.

⁴ Hartley, *Koll. Zeit.*, 1939, **88**, 22.

⁵ Murray, *Trans. Faraday Soc.*, 1935, **31**, 206.

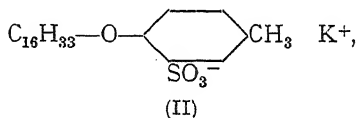
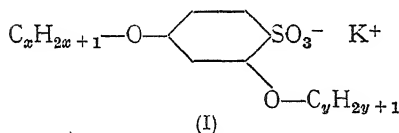
⁶ Hartley and Runnicles, *Proc. Roy. Soc. A*, 1938, **168**, 420.

⁷ Cf. Ward, *ibid.*, 1940, **176**, 412.

water to expel intruding paraffin-chains, and would therefore be less easily formed—*i.e.* only at a higher concentration. Now, if we retain the same amount of paraffin in an ion, but replace the straight chain by two approximately equal branches, we shall greatly reduce the maximum size of micelle of the normal type which can be formed, because this is limited by the necessity of some chains being able to reach from the surface to the centre.⁶ The *a priori* probability of the chains attached to an ionic group in the surface being found wholly inside the micelle will also be reduced. The micelle-forming mechanism will therefore be much less available. On the other hand, the inconvenience to the water molecules of retaining the paraffin intruding between them will be somewhat reduced, since the double chain is already part way to assuming the huddled-together form into which, according to Langmuir,⁸ an isolated paraffin molecule in water will be driven.

We should expect, therefore, that a salt with double- or branched-chain ions will have rather less interfacial activity, at the same single ion concentration, than a corresponding straight-chain salt, but that, if it is sufficiently soluble, the former will continue to reduce I.T. with increasing concentration beyond the concentration at which reduction by the latter ceases. Adequate single-ion solubility should be assured by the more awkward shape of the ions, leading to a weaker crystal structure.

Mainly with a view to investigating the predictions outlined above, a suitable series of compounds was prepared by sulphonation of di-alkyl ethers of dihydric phenols.⁹ We have the resorcinol series of general formula (I), which we will designate by R (10, 6), etc., the numbers denoting values of x and y . These are not respective, each compound where $x \neq y$ being a mixture of two isomers not separated. Further compounds are the corresponding pyrocatechol series—C (8, 8), etc.—



and the hydroquinone series—Q (8, 8), etc. The latter possesses some highly abnormal properties which require further investigation before any lucid account of them can be given. For comparison, a suitable straight chain salt (II)—*p*-T (16), was selected, having the convenience of being readily soluble at room temperature. The same geometrical principle is embodied in certain technical compounds—*e.g.* Tergitol 4 and 7,¹⁰ and Aerosol O.T.¹¹ Further interest is added to the subject by the investigations of Stanley, Adams and collaborators¹² on the effect of many branched-chain carboxylic acids on acid-fast bacteria. Unfortunately, the ill-defined conditions of solution of the acids in this work makes it impossible to say whether the above theory has any relevance. It seems, however, opportune to publish this short note, although my own experimental work has been interrupted while still far from complete.

⁸ Langmuir, Alexander's *Colloid Chemistry*, Vol. I (New York, 1926), 525.

⁹ Hartley, *J. Chem. Soc.*, 1939, 1828.

¹⁰ *Ind. Eng. Chem.*, 1937, 29, 1234. B. Pat. 440539.

¹¹ B. Pat. 440568.

¹² *J. Pharm. and Exp. Therap.*, 1932, 45, 121.

Compounds R (6, 8), R (8, 8), R (10, 8), R (10, 6), and C (8, 8) are all obtainable in clear solution in water at concentrations higher than the critical for *p*-T (16), and are therefore suitable for test of the theory. There is, however, no abnormal increase of temperature coefficient above a well-defined temperature, and the solubility at 100° C. is still only a few per cent. Parallel with this, other evidence of typical micelle formation is absent, *e.g.* there is no obvious solvent action of the clear solutions on azobenzene,¹³ and no marked effect on the equilibrium of suitable buffered indicators.¹⁴ Only two of these compounds have been obtained in well-defined crystalline condition—R (8, 8) and C (8, 8)—and crystals of both disperse spontaneously in water, those of the former in the cold and of the latter on heating, to give milky suspensions if the solubility is exceeded. The second phase in these suspensions, and in those of the others of the series, is certainly a liquid one, though only with care obtainable except as a fine emulsion. This property is of significance in the present connection in that it suggests that there is a limit to the concentration of amphipathic molecules obtainable in the free state in water more fundamental than the one which we have removed by changing from a straight to a branched chain—the water may dissolve in the salt rather than the salt in the water.

Interfacial tensions were measured by the stalagmometer method

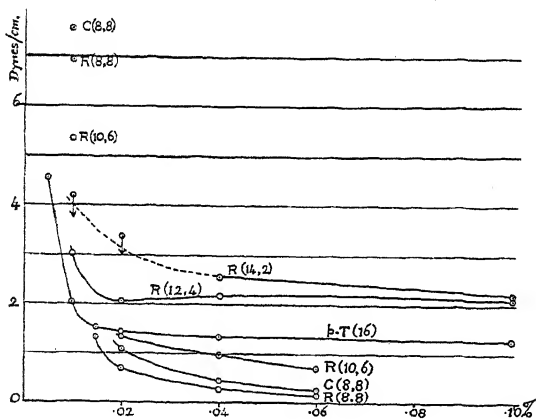


FIG. 1.

tions, however, the order is reversed. Micelle formation takes increasing toll of single ion concentration in the same order as the surface activity of the latter. In the two di-octyl compounds, in which tendency to aggregation is presumably least, the reduction of I.T. is most persistent. With R (8, 8) measurements became impossible above 0.06 % owing to counter-currents of oil and water setting up spontaneously in the capillary tip of the stalagmometer, with attendant emulsification. Only by allowing the oil to stream rapidly through the dry capillary before immersion in the solution and avoiding any interruption of the stream was the measurement at this concentration possible.

It was of interest to see how low the I.T. could be brought and still be measured by this method. To this end a mixture of cyclohexane and carbon tetrachloride was made up, having a density only 0.0413 above that of water. In this way the more convenient down-flow stalagmometer

between clear solutions of these salts at 25° C. and simple non-polar liquids. Results for cyclohexane are given in the figure. They provide a striking verification of the theoretical prediction. If we consider the sequence of effectiveness at the lowest concentration, the advantage lies with the straight-chain salt and the more unsymmetrical double-chain salts. At

¹³ Cf. Hartley, *J. Chem. Soc.*, 1938, 1968.

¹⁴ Cf. Hartley, *Trans. Faraday Soc.*, 1934, 30, 444; Hartley and Roe, *ibid.*, 1940, 36, 101.

could be used, larger drops obtained and less tendency for inversion inside the capillary. The I.T. of the mixture against pure water was 45.0 dynes/cm. and against 0.04 % solutions of *p*-T (16), R (10, 6) and R (8, 8) values of 1.13, 0.49, 0.12 dynes/cm. respectively were found: at 0.06 %, 1.12, 0.36, 0.07, and at 0.08 %, 1.12, 0.26, 0.04 dynes/cm.

Consistent with these extremely low, rapidly attained I.T.'s, it was observed that R (8, 8) solutions of concentration 0.12 %, the most concentrated clear solution of this compound obtainable at room temperature, emulsified various oils extremely easily. Gentle hand shaking in an open test-tube was adequate to produce emulsions stable for at least several weeks. Whether these emulsions will be more or less permanent than those prepared by more vigorous shaking with solutions of straight chain salts was not decided, and is of no direct significance in the present connection, since many factors other than low I.T. contribute to the stability of emulsions.

The measurements of I.T. were made by running the non-polar liquid from the stalagmometer into the solutions. The solutions wet glass preferentially and the drops therefore form from the inside circumference. It was found preferable to use tips obtained by simple fracture of capillary tube, without grinding, care being taken to choose normal fractures. The tips were sealed on to a length of micropipette. A constriction was made at the seal so that external pressure was necessary to secure sufficient flow, which was controlled by variation of the pressure, supplied by a pair of aspirators. The tips used in two up-flow stalagmometers had inner radii of .822 and .377 mm., determined by weight of mercury thread in the tube. Measurements for benzene against water gave values of 34.1 and 34.8 dynes/cm. respectively, in good agreement, in view of the unsuitability of these tips for such high tensions, with the value of 34.18 carefully determined by Harkins and Humphrey.¹⁵ For cyclohexane against water, values of 49.3 and 50.9 were obtained. The tip for the down-flow instrument had inner radius = .367 mm. Results were calculated using the correction tables of Harkins and Brown (I.C.T.). No difficulty was experienced in reducing the rate of flow sufficiently for there to be no further change of drop-volume with rate, due to time required for diffusion into the interface, except with the compound R (14, 2), which showed a persistent drift of I.T. with rate of flow at concentrations below .04 %. At the lowest concentrations the measurements were somewhat tedious. The second cause of variation with rate, mentioned by Powney and Addison,¹⁶ namely diffusion across the interface into the oil phase, which can produce more serious and protracted variation, was not observed in the case of cyclohexane or its mixture with carbon tetrachloride. With benzene, on the other hand, in which these potassium salts are fairly soluble, constant I.T.'s were never attained. Values interpolated for constant rate of formation of interface showed, however, the same sequence of effectiveness of the various salts at various concentrations as was found with cyclohexane.

This work was carried out in the Ralph Forster and William Ramsay Laboratories at University College, London, as part of a Royal Society Warren Fellowship programme.

*Livery,
Winterslow,
Wilts.*

¹⁵ *J. Am. Chem. Soc.*, 1916, **38**, 228.

¹⁶ *Trans. Faraday Soc.*, 1938, **34**, 356.

THE ORIENTATION AT THE OIL/WATER INTERFACE OF ESTERS AND THEIR DIGESTION BY PANCREATIN.

By J. H. SCHULMAN.

Received 23rd December, 1940.

(a) Physical Chemical Considerations.

Orientation of Aliphatic Esters and OH⁻ ion Adsorption at Air/Water and Oil/Water Interfaces.

It has been shown by Alexander and Schulman¹ that the rate of hydrolysis of monolayers of long-chain esters spread at the air/water interface was governed by the mutual orientation of the acid radical chain to the alcohol radical chain, rotation taking place around the C—O linkage. Thus when the two hydrocarbon chains are adlined together termed the *cis* position, unrestricted approach to the positive ketonic carbon atom by the OH⁻ ion can take place, whereas when the two hydrocarbon chains are orientated opposite one another, termed the *trans* position, approach of the OH⁻ ion is very restricted even by two (CH₂) groups. Rates of hydrolysis of the esters in the two described positions can vary as much as thirty times. These results have an interesting bearing on the investigations of G. C. Williams,² who examined the electrophoresis of aliphatic ester emulsions as a function of the pH.

Williams describes three distinct electrophoretic types which behave in a markedly different manner with the pH.

Type I which shows only small increasing changes of mobility with rising pH.

Type II, which shows only small changes of mobility until pH 8 is reached, when a most marked increase in mobility occurs.

Type III, which shows an increasing change in mobility over the whole range of pH joining type II at a pH of about 9. Williams hesitates to interpret his results on existing evidence, but to the author a ready explanation of his results seems possible.

All compounds that follow curves of type I act as if they are esters in the *trans* configuration at the air/water interface—that is with a CH₂ group either end of the molecule. Thus they behave like the hydrocarbons. It is perhaps better, since with this type one is dealing with solids, to make a comparison with their crystal structure and not their orientation at the air/water interface. Thus cetyl palmitate almost certainly crystallises in the *trans* position and not in the hairpin form, as is found at the air/water interface. Films of cetyl palmitate only stand pressures of 0.4 dynes/cm. and are consequently in a very labile form. Ethyl stearate, another example of this type, is clearly in the *trans* form, both in films and crystals.

¹ *Proc. Roy. Soc. A*, 1937, **161**, 115; and Alexander and Rideal, *ibid.*, 1937, **163**, 70.

² *Trans. Faraday Soc.*, 1940, **36**, 1042.

Examples quoted for type III are known to exist at the air/water interface in the form of films whose molecules are definitely in the *cis* form, when the film is in equilibrium with a lens of ethyl myristate or laurate, and not in the condensed state as suggested by Williams. Substances which follow curves of type II exist at the air/water interface in the form of vapour films. Thus, with these substances no mutual orientation can occur at the interface. The molecule is more than likely, owing to the small adhesion between the small hydrocarbon chains, to be in the *trans* configuration*. At pH 8 a sufficient concentration of OH^- ions is present in the aqueous solution to anchor on to the positive ketonic C^+ and orientate the molecules at the interface so that they now behave as those in type III, molecules of type III achieving their orientation at the interface by means of the long hydrocarbon chain.

Thus, molecules of type I have the positive ketonic carbon protected by a small hydrocarbon chain; those of type II are unable to orientate and absorb OH^- ions until the concentration of the OH^- ions is sufficiently high (*i.e.* pH 8), those of type III can absorb OH^- ions gradually over the whole range of pH . This brings the results obtained by the Electrophoresis experiments at the oil/water interface into direct corroboration with the results obtained by the Monolayer technique at the air/water interface. The acetate esters are a special case, as here the acetyl CH_3 group has free rotation around either the $C-O$ or CH_2-O bond. It is perhaps significant that there are two special crystal forms of long-chain acetates, one form crystallising in double layer lattices and one in single layer lattices. From a study of multilayers a possible explanation is that when the polar group is protected by the hydrocarbon CH_3 group, single layer lattice crystals grow, but when the polar groups are free to associate, double layer lattice crystals or multilayers can grow or be built up. There is evidence from Williams' results on the OH^- adsorption at the solid/water and oil/water interface, that the acetyl CH_3 group by rotation is restricting or permitting approach to the ketonic carbon atom.

(b) Biological Considerations.

Steric Factors.

Since steric factors play such a large part in hydrolysis and adsorption of OH^- ions on to esters at the air/water or oil/water interface, it could be anticipated that similar factors would function in the digestion of these esters by lipoclastic ferments.

For this purpose a series of aliphatic and other esters were collected, each ester only varying in the number of carbon atoms in the acid radical chain or alcohol radical chain. It has already been shown in the previous section, how only by the addition or removal of one carbon atom in an aliphatic chain, alterations in the associations of the alcohol radical and acid radical hydrocarbon chain took place, thus affording protection or unrestricted approach of OH^- ions to the active ketonic carbon in the polar group. That this fact also functions in restricting the approach of a biological catalyst as found in pancreatin can be seen in a most striking manner in Table I.

It can be seen that there is a great difference, due to the length of the

* *J. Chem. Soc.*, 1939, 177.

TABLE I.

5 C.C. H₂O + 5 DROPS BROM. THYMOL BLUE +
1 C.C. ESTER + 0.2 G. PANCREATIN NEU-
TRALISED TO BLUE WITH N/10 NaOH.
24 Hours at 17° C.

Solubility of Ester in Water.	Ester.	NaOH c.c. N/10.
0.68 %	Ethyl butyrate	2.75 c.c.
0.167 %	Propyl butyrate	2.5 c.c.
i.s.	Benzyl propionate	2.25 c.c.
0.08 % (iso)	Amyl (n) propionate	1.40 c.c.
sl. s.	Butyl propionate	1.40 c.c.
0.063 %	Ethyl caprylate	1.10 c.c.
0.054 %	Amyl butyrate	0.80 c.c.
0.18 %	Amyl acetate	0.75 c.c.
0.237 % (n)	Ethyl iso-valerate	0.30 c.c.
i.s.	Amyl caproate	0.20 c.c.
sl. s.	Amyl valerate	0.10 c.c.
0.08 %	Ethyl benzoate	0
i.s.	Amyl benzoate	0

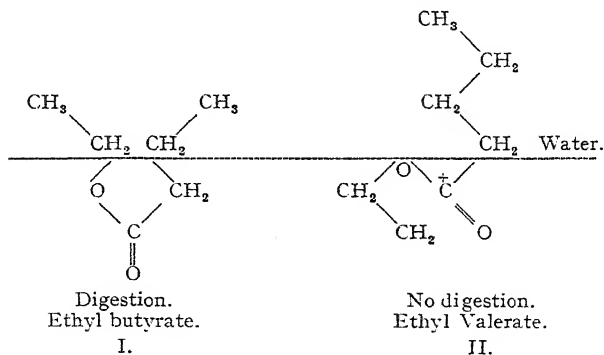
alcohol or acid radical chain; the acid radical playing the more important part. Thus, even with a very short alcohol radical chain (*i.e.* ethyl) nearly complete inhibition of the digestion of the ester sets in when the acid radical chain consists of 5, 6 carbon atoms or C₆H₅, the digestion of the esters setting in again when the acid radical chain consists of 8 carbon atoms.

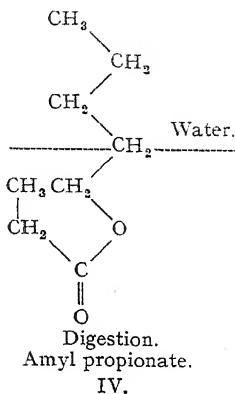
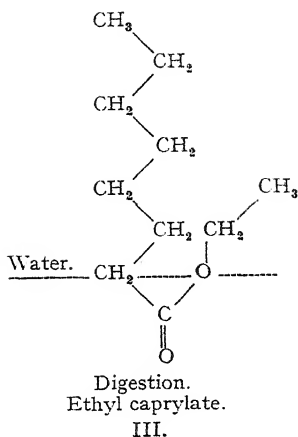
The length of the hydrocarbon chain of the alcohol radical has no influence over the

indigestible region, but causes some inhibition over the short and long acid radical hydrocarbon chain region.

Digestible. 2—3—4	Indigestible. 5—6—C ₆ H ₅	Digestible. 8 Acid Radical.
affected by length of alcohol radical hydrocarbon chain.	unaffected by length of alcohol radical chain.	affected by length of alcohol radical hydro- carbon chain.

Thus butyl and amyl butyrate are more difficult to digest than ethyl butyrate or amyl caprylate than ethyl caprylate. The importance of the nature of the acid radical or alcohol radical chain is well demonstrated by ethylbenzoate or ethyl valerate which are indigestible as compared to benzyl propionate or amyl propionate which are readily digested by pancreatin. An attempt has been made to depict the possible orientations which would account for the experimental results. These configurations are taken from Alexander and Schulman.





It is difficult at the moment to understand why a lengthening of the acid radical chain from 6 to 8 should influence the orientation of the ethyl group. The C 8 chain can perhaps just bring about orientation at the interface to enable the polar group to sit in the *cis* configuration as the long chains esters up to C 14 certainly do, and thus be digestible. It is perhaps significant that the indigestible esters fall into type II compounds of G. C. Williams, but this is not fully established yet.

Summarising these results it can be seen :

(1) That esters whose alcohol and acid radical chains are less than 5 carbon atoms long cannot orientate themselves at the interface, and are therefore easily digestible (Picture I).

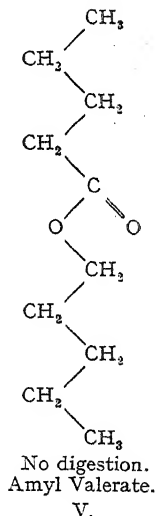
(2) Esters whose acid radical chain is 5, 6 or C_6H_5 carbon atoms and alcohol radical 2 carbon atoms or more, are indigestible (Picture II) (Type II, G. C. Williams).

(3) Lengthening the acid radical chain to 8 carbons or more to 14 enables the ethyl group of the alcohol radical to orientate itself into the *cis* configuration, type III, G. C. Williams (Picture III). These esters are therefore easily digestible.

(4) The inverse of Class II brings into play the acetate configuration of Alexander and Schulman (Picture IV) which are therefore easily digestible.

(5) If both the acid and alcohol radicals are 5 carbon atoms long or more, then Picture V seems the most like configuration, which would account for the indigestion of these esters by pancreatin.

The surprising results of (2) and (3) may be accounted for by the difference in solubility or association of component parts of an orientated molecule at the interface with the unorientated molecules in the interior. In Table I is quoted the solubility of the esters with water, which apparently has no bearing on the phenomenon observed.



That these steric factors may play an important part in the hydrolysis of esters with caustic soda in general has been demonstrated by H. S. Levenson and Hilton A. Smith on the kinetics of the saponification of ethyl esters of several phenyl substituted aliphatic acids.⁵

The Influence of Simple Ionic Polar Groups on the Lipoclastic Action of Pancreatin.

The complex formation of long-chain hydrocarbon ions with monolayers of chemicals found in the cells such as cholesterol, esters, fatty acids and proteins, has been studied by Schulman and Rideal,³ together with their possible biological analogies. Very recently Anson⁴ has studied the action of certain detergents on various proteins, and more especially sodium dodecyl sulphate on egg albumen in relation to oxidation of the S—H groups by dilute ferricyanide solutions to the S—S group. It has been known for a long time that fatty acids and bile acids enhance the action of pancreatic lipase. This is well demonstrated in Table II, where a whole series of dodecyl ionic salts have been studied in a concentration of 1 in 1000 on 0.2 g. of pancreatin. It is shown that long-chain amines and quarternary bases behave in a similar fashion to the fatty acids and bile acids in enhancing the lipoclastic action of pancreatin, but the long-chain sulphates and sulphonates are very strong inhibitors.

TABLE II.

6 C.C. H_2O , 1 : 1000 AGENT, 1 C.C. ETHYL BUTYRATE, 0.2 G. PANCREATIN, 5 DROPS BROM THYMOL BLUE. TEMP. $18.5^\circ C$.

		Agent.	Time 42 hours. NaOH N/10.
		Sodium dodecyl sulphate	0.3 c.c.
		Sodium taurocholate	4.5 c.c.
		Sodium dodecyl sulphonate	1.35 c.c.
		Sodium laurate	4.80 c.c.
		Hexadecyl pyridinium bromide	3.65 c.c.
		Dodecyl amine HCl	5.70 c.c.
		Hexadecyl trimethyl ammonium bromide	5.5 c.c.
		Sodium dodecyl sulphate + 100 mg. $BaCl_2$	0.90 c.c.
		Blank	3.05 c.c.
24 hrs.	{	Sodium hexadecyl sulphate (24 hours)	0.5 c.c.
		Sodium hexadecyl sulphate + $BaCl_2$	1.90 c.c.
		Blank	1.85 c.c.
		Sodium dodecyl sulphate 100 mg. with or without $BaCl_2$	0.25 c.c.

The inhibition of the ferment by the long-chain sulphates is to a certain extent reversible in dilute solutions, but not in strong solutions. Thus if a $BaCl_2$ solution be added to the sodium dodecyl sulphate 1 : 1000 solution a partial reaction recommences after a two hour incubation of the long-chain sulphate with the ferment. Whereas with the sodium hexadecyl sulphate, which probably owing to its reduced solubility is less of an inhibitor, complete regeneration with a $BaCl_2$ solution takes place. From a study of mixed monolayers and monolayer penetration experiments and emulsions, the association of the long-chain compounds with esters has been shown to be very small. Thus the enhancement of

³ *Proc. Roy. Soc. B*, 1937, **122**, 29; *Nature*, 1939, **144**, 100.

⁴ *J. Gen. Physiol.*, 1940, **23**, 247.

⁵ *J.A.C.S.*, 1940, **62**, 2324.

the ferment action would appear to be due to protein dispersion. Most substances that disperse proteins such as sodium benzoate appear to activate the ferment. It would appear that these long-chain compounds, which most certainly attack protein monolayers and not ester monolayers, are attacking and dispersing the protein component of the ferment, and the long-chain sulphate some part of the prothetic group, or perhaps separating component parts of the ferment complex as suggested by the work of Peters and Wakelin ⁶ on ovoverdin and Sreenwasaya and Pirie ⁷ on virus.

Experiments.

The experiments recorded in this communication are only of a provisional and preliminary nature.

The esters are chiefly redistilled B.D.H. samples. Various samples of powdered pancreatin were used, made by Merk or Harrington. No purification by adsorption was undertaken. The samples varied slightly in potency, but gave identical differential results on the digestion of the esters. The long-chain hydrocarbon ionic compounds were pure specimens, especially the long-chain sulphate compounds, which acted in the exceptional manner described in the paper. Identical results were obtained using specimens from different sources.

The reactions were carried out at room temperature in unbuffered solutions, therefore in acid pH . It was found that under these conditions the lipoclastic activity of pancreatin was not seriously impaired after long periods. In alkaline solutions at higher temperatures the lipoclastic activity decreased rapidly probably from auto-digestion by the proteolytic ferments present.

Summary.

Direct analogies have been drawn from observations on the adsorption of OH^- ions on the ester molecules orientated at the air/water interface to the adsorption of the OH^- ions at the oil/water interface.

These results have been used to explain the curious specific action of the lipoclastic ferment in pancreatin on its digestion of aliphatic esters. The esters varied in the number of carbon atoms attached to the alcohol and acid radical hydrocarbon chains.

Further, the action of long-chain hydrocarbon ionic salts was studied on the rate of digestion, by the lipoclastic ferment in pancreatin, of a long-chain ester.

My acknowledgments are due to the Medical Research Council for a personal grant, and to Professor E. K. Rideal for helpful criticism.

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⁶ *Biochem. J.*, 1938, **32**, 2290.

⁷ *Ibid.*, 1707.

THE EFFECT OF pH UPON THE ELECTROPHORETIC MOBILITY OF EMULSIONS OF CERTAIN HYDROCARBONS AND ALIPHATIC HALIDES.

By W. DICKINSON.

Received 5th November, 1940.

It has long been known that droplets of an oil, dispersed in water, carry an electrical charge which is usually negative. This charge is thought to be due to the adsorption of hydroxyl ions, and gives rise to an electrical double layer across the interface. Part of this fall in electrical potential across the interface gives rise to the electrokinetic effects which have been observed by a number of experimental methods. Considering the motion of an emulsion droplet under the influence of an applied electrical field, it is generally assumed that the inner part of the double layer on the aqueous side of the interface adheres to the droplet, while the outer part of the double layer is mobile with respect to the oil surface. The potential difference, ζ , across the mobile part of the double layer is responsible for the electrophoretic motion of the droplet through the aqueous phase. The electrophoretic mobility is almost proportional to the ζ potential.

The electrophoretic mobility of emulsions of a dispersed oil is dependent on various factors, the most important of which are, assuming the temperature to be constant, (1) the composition of the oil phase, (2) the pH of the aqueous phase, and (3) the concentration and valency of the ions, particularly of the cations, dissolved in the aqueous phase. The last factor has been the subject of numerous researches in the past, and some theoretical work has been published to account for the observed phenomena. The first two effects have, however, received considerably less attention from colloid chemists, and very little work of a systematic nature appears to have been carried out on these effects. Alty and Johnson¹ have investigated the effect of the substituent group in certain amides, acids, alcohols, etc., coating paraffin wax cylinders, upon the electrophoretic mobility of the cylinders, and found that the groups concerned had a decided specific effect on the mobility. In addition, Carruthers² has investigated the effect of the chemical composition of the oil phase of an emulsion upon the electrophoretic mobility, over the range pH 2 to pH 11.8. He found that an increase in chain length had no effect on the mobility of a substituted paraffin provided that no change of state occurred, and came to the conclusion that the mobility effect of the end group could be related to the "residual charge" associated with it. The residual charge, which arises from the unequal sharing of electrons between the group concerned, and the rest of the molecule, results in a net charge on the end group, which attracts or repels hydroxyl ions to the adsorption layer according to its sign. Thus, if the end group is associated with a net negative charge, hydroxyl ions are assumed

¹ Alty and Johnson, *Phil. Mag.*, 1935, 20, 129.

² Carruthers, *Trans. Faraday Soc.*, 1938, 34, 300.

to be repelled from the adsorption layer, reducing the negative charge at the interface. Hence, the electrophoretic mobility of emulsions of the appropriate compound is less than the mobility of emulsions of a compound whose end group is characterised by a zero residual charge. The work recorded in this paper may be considered to be an attempt to extend and replace some of Carruther's results.

Experimental.

Preparation of the Emulsions.

Three methods were used for preparing the dispersions. (1) 0.5 g. of the organic compound was dissolved in about 15 c.c. of hot alcohol, the resulting solution being slowly added, with vigorous stirring, to one litre of boiled distilled water at a temperature of about 98° C. Most of the alcohol was driven off on contact with the almost boiling water, but as some alcohol may still remain, it was verified in all cases for which this method was used that the remaining alcohol had no effect, by boiling a dispersion for over an hour and comparing the mobility of the resulting emulsion with that of an unboiled emulsion, and where possible, with the mobility of an emulsion prepared by the other two methods to be described.

(2) About 1 g. of the organic liquid to be emulsified was floated on the surface of 1 litre of distilled water, and steam at a pressure of 1½ m. of water was blown through a jet, 1 mm. in diameter, situated at the interface. The oil was quickly dispersed. Bondy and Söllner³ suggest that dispersion is effected by ultrasonic waves produced by the collapse of steam bubbles coming into contact with cold water.

(3) About 1 g. of the organic liquid was passed several times through a mechanical homogeniser with 1 litre of distilled water.

The Aqueous Phase.

It has already been mentioned that the mobility of a dispersed oil depends on the pH of the aqueous phase, and on the concentration and valency of the ions in this phase. For the case of negatively charged droplets it has been found that, while cations have a pronounced specific effect on the mobility, anions, with the exception of the hydroxyl ion, have much the same general effect on the mobility. Comparisons of electrophoresis data can only be made when the nature of the cation, and its concentration, together with the pH value of the aqueous phase are identical in the cases compared. The first two of these factors are known from the manner in which the solutions are made up, while the last is easily measured.

In the investigation of the effect of pH upon the mobilities of emulsions, the pH range used was from pH 2.0 to pH 11.8, while the cation concentration was maintained throughout at 0.01 N sodium ion. From pH 2.0 to pH 5.5, the pH was obtained by diluting 10 c.c. of 0.1 N NaCl, and the required amount of dilute hydrochloric acid with water, or stock emulsion, to 100 c.c. Although these solutions are unbuffered, the pH values could generally be repeated to 0.03 of a pH unit. From pH 5.5 to pH 11.8, the pH was obtained by the use of either phosphate or borate buffer. The highest pH obtainable is, of course, that of 0.01 N sodium hydroxide. It was found that, when both phosphate and borate buffers were used, the mobilities obtained agreed in the pH region covered by both buffers.

The pH values of the solutions used were frequently checked, using a glass electrode apparatus to measure pH values below pH 9.0, and a hydrogen electrode apparatus if the pH value of the solution was known to be greater than pH 9.0.

³ Bondy and Söllner, *Trans. Faraday Soc.*, 1935, **31**, 835.

The Mobility Determinations.

The moving boundary method of measuring electrophoretic mobility was used. The apparatus was similar to that described by Price and Lewis.⁴ All measurements were made at a temperature of 25.0° C., which was obtained by suspending the U-tube in a glass trough through which water from a thermostat was circulating. Both the supernatant liquid and the dispersion mixture used were of the same ionic composition, and in order to obtain sharp boundaries, 2 % of A.R. sucrose was added to the emulsion.

The Electrophoresis of Hydrocarbons.

Purification.

The careful purification of the organic compounds employed in work of the nature described in this paper is of the utmost importance, as it has been found that traces of impurities frequently have a large effect on the observed mobilities. The hydrocarbons investigated were *n*-octadecane, and paraffin wax.

The octadecane, as supplied by Fraenkel and Landau, had an iodine value of 3.7 and its emulsions had a mobility of 5.01 units (μ /sec./v./cm.) at p_H 9.0 in the presence of 0.01 N sodium ion. A number of methods of purification, such as repeated recrystallisations from alcohol, acetone, or treatment with concentrated sulphuric acid, gave rise to a product with a mobility of about 1.15 units at p_H 9.0 in each case, and this mobility was unchanged by further purification. This mobility was also confirmed by other workers in this laboratory, who purified the hydrocarbon independently. The method finally adopted for the purification of octadecane consisted of four recrystallisations from absolute alcohol, which yielded a product with a mobility of 1.14 units at p_H 9.0. The mobility was unchanged by further recrystallisations from alcohol, or by treatment with concentrated sulphuric acid, while the iodine value was reduced to a negligible value. The m.p. of the final product was 28° C.

The original paraffin wax was Baird and Tatlock's "specially selected" wax, m.p. 60° C. The wax was crystallised twice from benzene, after which it was shaken twice with hot, concentrated sulphuric acid at a temperature above the m.p. of the wax. Purification was continued by recrystallisation from alcohol, after the wax had been washed to neutrality by repeated shaking with hot water. The mobility of the wax was reduced to 1.19 from 1.55 units at p_H 9.0 by this treatment. The purified wax was then recrystallised twice from a mixture of alcohol and benzene. The mobility of the final product was 1.16 units at p_H 9.0. The wax had thus been purified to constant mobility, to within the experimental error, while the mobility obtained is similar to that obtained for octadecane at p_H 9.0.

The Electrophoresis Data for the Hydrocarbons.

The octadecane emulsions used were prepared by condensation from alcohol. It was verified that these emulsions gave the same mobility, at p_H 9, as emulsions prepared by the steam jet method, and by the mechanical homogeniser. The paraffin wax emulsions were also prepared by condensation from alcohol.

The data obtained for octadecane and paraffin wax are plotted in Fig. 1.

The mobility- p_H curve for paraffin wax differs only slightly from that of octadecane. Below p_H 6 the curves are identical, but they diverge slightly above this p_H value. The cause of this is unknown, but as the

⁴ Price and Lewis, *Trans. Faraday Soc.*, 1933, 29, 775.

maximum deviation is only of the order of 0.1 mobility units, the agreement can be said to be reasonably good. In view of the fact that paraffin wax consists of a mixture of hydrocarbons having odd and even numbers of carbon atoms it may be concluded either that the paraffins have a common end-group $-\text{CH}_3$ projecting into the aqueous phase or if any $-\text{CH}_2-$

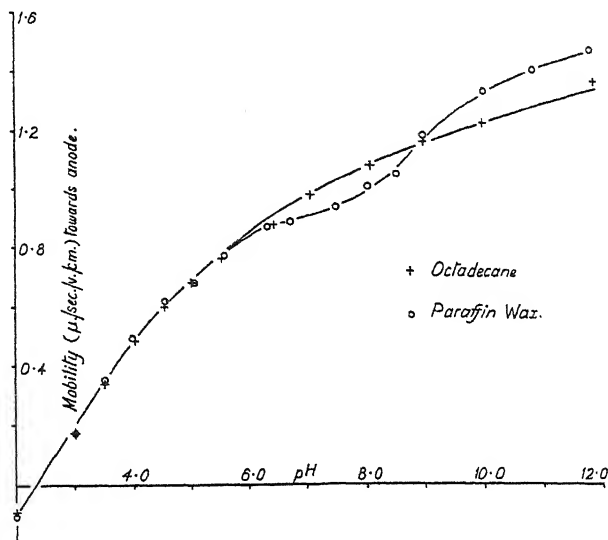


FIG. 1.—The effect of pH on the mobility of dispersions of octadecane, and purified paraffin wax, in the presence of 0.01 N sodium ion.

groups be likewise present the adsorption capacity of this group for hydroxyl ion is not distinguishable from that of the $-\text{CH}_3$ group. The second alternative would appear to be less probable than the first in view of Trillat's electron diffraction results. In either event the length of the chain embedded in the solid particle is immaterial.

The Electrophoresis of Aliphatic Halides.

Purification.

The methods used for the purification of the aliphatic halides were chiefly those of fractional distillation under reduced pressure, and crystallisation. The halides, all liquid at 25° C., investigated are: cetyl and octyl iodides, cetyl bromide, and cetyl, octadecyl, and lauryl chlorides. The method of purification depended, to some extent, on the halide used. For example, octyl iodide was repeatedly distilled under reduced pressure, over silver powder, until the mobility of its emulsions had attained a constant value at pH 9.0. Cetyl iodide was repeatedly recrystallised from a mixture of methyl alcohol and ether (*cf.* Smith⁵) until constant mobility had been attained. In each case, the halide concerned was purified to constant mobility at pH 9.0.

The Electrophoresis Data for the Aliphatic Halides.

The emulsions used were prepared both by the steam jet method and by condensation from alcohol. Emulsions of the same halide, prepared by both methods, gave identical mobilities at pH 9.0. The data obtained

⁵ Smith, *J. Chem. Soc.*, 1932, 737.

for the iodides and bromide are plotted in Fig. 2, while the data obtained for the chlorides are plotted in Fig. 3.

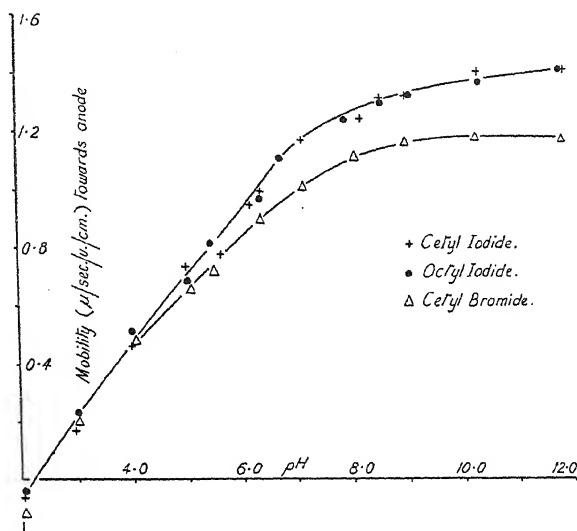


FIG. 2.—The effect of pH on the mobility of emulsions of cetyl iodide, octyl iodide, and cetyl bromide, in the presence of 0.01 N sodium ion.

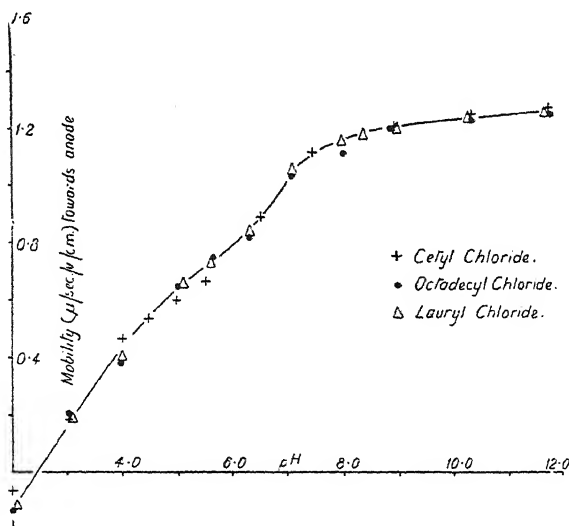


FIG. 3.—The effect of pH on the mobility of emulsions of cetyl, octadecyl and lauryl chlorides, in the presence of 0.01 N sodium ion.

Discussion.

The mobility- pH curves obtained are all of the same general type. The mobility increases with pH , rapidly in the lower pH region, but only

slowly for higher pH values, above pH 9.0. There is frequently an inflection in the curve at pH 6 to pH 7, the cause of which is unknown. As the mobility increases only slowly beyond pH 9, this region is the most suitable in which to compare the effect of various substituent groups on the electrophoretic mobility. Before discussing this effect it is desirable to account for the charge at the interface, and its variation with the pH of the aqueous phase.

Except for the lowest pH values, the emulsion droplets are negatively charged. The exact mechanism for the formation of the negative charge is not yet clearly understood, but it is probably connected with the interrelated properties of hydrogen ions, hydroxyl ions, and the water molecules which cover the aqueous side of the interface. It is generally assumed that the negative charge is due to the adsorption of hydroxyl ions, brought about by one of the following two mechanisms, or a combination of the two.

The hydroxyl ions may be adsorbed directly from the aqueous phase, in which case the number of hydroxyl ions adsorbed per unit area will depend on the hydroxyl ion concentration in the bulk of the aqueous phase, *i.e.*, on the pH of this phase. As the pH is increased, the primary charge density will increase, and at high pH values will approach a maximum as the surface becomes saturated with hydroxyl ions. If, as the pH is increased, the cation concentration is maintained constant, *i.e.*, the ionic strength of the aqueous phase and the thickness of the double layer are maintained almost constant, it would be expected that the electrophoretic mobility would follow, qualitatively, the course of the primary charge density. If this mechanism holds, an examination of the electrophoretic data available indicates that hydroxyl ion adsorption possesses some unusual characteristics. For example, saturation of the surface by hydroxyl ions appears to occur at the low concentration of about $10^{-5} N$ (pH 9.0), while adsorption appears to be appreciable at the really minute hydroxyl ion concentrations of about 10^{-10} – $10^{-9} N$ (pH 4 to 5).

The second mechanism for the primary adsorption of hydroxyl ions is that the oil surface should first adsorb a complete unimolecular layer of water molecules, some of these subsequently ionising, the hydrogen ions migrating into the aqueous phase, leaving the corresponding hydroxyl ions adsorbed at the interface. The degree of ionisation of the water layer will depend on the pH of the aqueous phase; as the pH increases the degree of ionisation will increase, so that the density of adsorbed hydroxyl ions will be increased. Eventually, a stage will be reached when no further ionisation takes place as the pH is increased, corresponding to saturation of the surface with hydroxyl ions. Both mechanisms appear to lead to the same ultimate results. In favour of the second mechanism, it may be mentioned that there is a certain amount of evidence, from other sources, that a layer of pure water exists at the surface of aqueous electrolyte solutions. Surface and interfacial tension measurements carried out on salt solutions indicate that there is a deficiency of salt at the interface compared with the bulk salt concentration. Furthermore, Bouhet,⁶ studying the elliptical polarisation of light reflected from the surfaces of salt solutions, came to the conclusion that the surface layer consisted of pure water. March⁷

⁶ Bouhet, *Ann. Physique*, 1931, **15**, 5.

⁷ March, *Ann. Physik*, 1927, **84**, 605.

calculated that observed ζ potentials were at least ten times too small to account for the stability of colloids, and proposed that the particles were surrounded by a protecting skin of water. Müller⁸ has developed this view, and suggested that the electrical field at the interface gives rise to the film of solvent by electrostriction.

Carruthers² from the results of his preliminary investigation into the mobility effect of polar groups came to the conclusion that the mobility could be correlated, in a qualitative way, with the residual charge on the end group. The residual charge can be obtained from a knowledge of the dipole moments of the individual links of the molecule, together with the lengths of these links, as shown by Sidgwick.⁹ Table I

TABLE I.*

	Moment $E \times d$ (Debyes).	Distance d (Å).	$E \times 10^{10}$ (e.s.u.).	$E/e = F$.
H—C	0.2	1.14	0.18	0.04
C—Cl	1.7	1.74	1.0	0.21
C—Br	1.6	1.90	0.8	0.17
C—I	1.4	2.12	0.7	0.15

* E = the charge on either atom in e.s.u.

d = the distance between the two atoms in Ångstrom units.

e = the electronic charge.

F = the residual charge associated with either atom.

contains a selection of residual charges, taken from Sidgwick's book. For each link, the positively charged atom is given first.

As an illustration, consider an emulsion of a long chain aliphatic compound, the molecules of which possess a hydrophilic group at one end of the chain. At the interface, the organic molecules will probably be orientated so that their chains lie side by side, while the hydrophilic groups project towards the aqueous phase. The hydrophilic group will be associated with a residual charge, either positive or negative, and the presence of the resulting sheath of charges at the interface will affect hydroxyl ion adsorption. Thus, a negatively charged end group will reduce hydroxyl ion adsorption, and hence the electrophoretic mobility by repelling hydroxyl ions from the interface, or alternatively, by reducing the degree of dissociation of the adsorbed water film. The forces involved will be of a comparatively short range nature. In the case of a paraffin hydrocarbon, the residual charge of the end $-\text{CH}_3$ group is zero. In the case of the alkyl halides, it is not definitely known whether the end group $-\text{CH}_2\text{X}$ is orientated towards the aqueous phase. Adam¹⁰ has pointed out that the halide group has no appreciable attraction for water, as shown by the fact that alkyl halides do not form films on water, and this has been confirmed by the contact angle measurements of Adam and Jessop.¹¹ The halide molecules are therefore not necessarily orientated steeply at the interface, with the halide group projecting towards the aqueous phase. If the halide group projects away from the interface, it would be expected that the halide

⁸ Müller, *J. Physic. Chem.*, 1935, **39**, 743.

⁹ Sidgwick, *The Covalent Link in Chemistry*, 1933, p. 154.

¹⁰ Adam, *The Physics and Chemistry of Surfaces*, 1938, p. 187.

¹¹ Adam and Jessop, *J. Chem. Soc.*, 1925, 1863.

emulsion would have a similar mobility to that of a hydrocarbon emulsion, because of the similarity in the nature of the interfaces. This would also be expected to be the case if the halide molecules lie flat at the interface, because both the negatively charged halide atom, and the adjacent positively charged carbon atom would lie in the surface, resulting in a group of zero residual charge, while most of the surface, occupied by the hydrocarbon chains, would be similar to the surface presented by a hydrocarbon. If, however, the organic molecules are orientated steeply to the interface, with the halide atom projecting towards the aqueous phase, the negative halide atoms will be nearer to the interface than the corresponding positively charged carbon atoms, and the end group will thus carry an effective negative charge. In this case, it would be expected that the mobility of the halide emulsion would be lower than that of a paraffin hydrocarbon emulsion, because of the effect of the negatively charged end group. Also, it would be expected that emulsions of the chloride would have a lower mobility than emulsions of the bromide, which in turn would have a lower mobility than emulsions of the iodide, because of the increasing residual negative charge on the halide atom in the series iodide, bromide, chloride. The mobilities of octadecane, the alkyl chloride, alkyl bromide, and alkyl iodide, at pH 11.8, are given in Table II.

TABLE II.

Compound.	Octadecane.	Alkyl Chloride.	Alkyl Bromide.	Alkyl Iodide.
Mobility at pH 11.8.	1.34	1.24	1.16	1.39

All the mobilities lie within a limited range. As expected, the mobility of the chloride is less than that of the iodide, but the mobility of the bromide is unexpectedly lower than that of the chloride. In comparing the mobilities of the halides with that of octadecane it must be remembered that the halides investigated are liquid at 25° C., while octadecane is solid at this temperature, and therefore the hydrocarbon and halide measurements may not be comparable. In this connection, Williams¹² has investigated the electrophoretic mobility of dodecane, which is a liquid hydrocarbon, and found that its mobility was appreciably greater than that of octadecane, *viz.*, 3.18 at pH 11.8. It appears, therefore, that the halide molecules at the interface orientate so that their halide groups project towards the aqueous phase.

Summary.

1. The effect of the pH of the aqueous phase upon the electrophoretic mobility of emulsions of certain hydrocarbons and aliphatic halides, in the presence of 0.01 N sodium ion, and at 25° C., has been investigated over the range pH 2.0 to pH 11.8.

2. In each case, the emulsions carry a small positive charge in the lowest pH values, but as the pH is increased the charge is reversed while the pH is still small, and on increasing the pH still further, the negative charge increases and finally attains an almost constant value above pH 9.

¹² Williams, *Trans. Faraday Soc.*, 1940, 36, 1042.

3. It is pointed out that the mobility effects of the various substituent groups are best compared in the alkaline region, where the curves have flattened off, and run nearly parallel to each other.

4. The source of the negative charge on the particle is discussed in relation to the effect of pH on the charge.

5. The effect of the nature of the end group upon the mobility of emulsions of the appropriate compounds is discussed in the light of the residual charge on the end-group.

The author wishes to express his indebtedness to Professor W. C. M. Lewis, under whose supervision the above research was carried out.

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ELECTROPHORESIS OF COMPLEX PARTICLES AS A FUNCTION OF pH : EFFECT OF STEARIC ACID IN ESTER PARTICLES.

BY G. GROWNEY.

(Communicated by W. C. M. LEWIS.)

Received 8th October, 1940.

Although various workers have investigated the effect of soaps on the mobility of emulsion particles no attempt has been made to ascertain the electrophoretic behaviour under standardised conditions of oil droplets containing various amounts of fatty acid.

In the following paper the system examined is an emulsion in which each droplet is chemically complex, consisting of an ester in which is dissolved a certain amount of fatty acid—stearic acid—itself sparingly soluble in water. An examination is made of the effects produced by a variation in pH of the aqueous phase on the electrophoretic mobility of the emulsion in the presence of 0.01 N sodium chloride or other univalent salt, the purpose of the salt being to maintain a constant thickness of the double layer.

A comparison is made between the electrophoretic mobility- pH curves of the two separate components and those of the complex droplets.

Experimental.

The electrophoresis measurements were carried out macroscopically in the moving boundary apparatus described by Price and Lewis¹ and subsequently by Roberts. The apparatus is capable of accurate temperature control and the measurements were made at 25° C.

pH values were determined by a glass electrode at 25° C. in an oil thermostat. The results are accurate, for buffered solutions, to 0.01 pH unit. For unbuffered solutions the error is ± 0.01 unit up to pH 5 and ± 0.05 unit between pH 5 and 7. For pH values greater than 9, the glass electrode is unsuitable and a hydrogen electrode is used. The results are accurate to 0.01 pH unit.

¹ Price and Lewis, *Trans. Faraday Soc.*, 1933, 29, 775.

Purification of the Materials.

The esters used were ethyl laurate (liquid) and ethyl stearate (solid). The ethyl laurate, supplied by B. D. H., was a colourless liquid with a pungent odour. It was purified by shaking with potassium carbonate and then with water and was distilled under reduced pressure after separating from the aqueous medium.

The ethyl stearate was kindly supplied chemically pure by Mr. G. C. Williams, of this laboratory.

The stearic acid used was purified by crystallisation from pure alcohol. In all cases the purification was carried out until constant mobility was attained. In our experience this is a highly sensitive test.

Preparation of the Dispersions.

A 0.1 % solution of stearic acid in ethyl laurate was obtained by weighing out 0.01 g. of stearic acid and adding to it 10 g. of ethyl laurate. On warming the mixture the acid dissolved. From this stock material mixtures containing 0.04, 0.05 and 0.06 % of stearic acid were obtained by dilution with the ester.

In making dispersions of these "oil"-acid mixtures the mechanical homogeniser was used to effect emulsification. The oil-acid mixture was passed through the homogeniser about fifty times so that the droplets attain uniform size. If the oil was not passed through the homogeniser a sufficient number of times the boundaries in the U-tube were diffuse.

Mixtures of 1 % stearic acid in ethyl laurate and ethyl stearate were made up at room temperature and in order to make the mixtures more homogeneous they were heated above the melting-point of stearic acid and maintained at this temperature (70° C.) during emulsification. The mechanical homogeniser could not be used as the molten stearic acid reacted with the metal of the homogeniser.

To emulsify the mixtures while hot the steam-jet method was used. About 1 g. of the heated mixture was floated on the surface of a litre of distilled water maintained at a temperature of 70° C. and steam at a pressure of $1\frac{1}{2}$ metres was blown through a jet 1 mm. in diameter situated at the oil-water interface. The mixture was quickly dispersed and the emulsion cooled.

Before carrying out any measurements the emulsions were left overnight. The mobility was found to be the same on standing four or five days although the concentration of the emulsion had diminished.

The Aqueous Phase.

It is well known that the electrophoretic mobilities are dependent on the ionic composition of the aqueous phase and consequently it is important to keep the ionic composition of the aqueous phase constant as far as possible throughout the pH range. Throughout the present work the mobilities were determined in the presence of 0.01 N sodium ion. Between pH 2 and pH 7 both dispersion and supernatant liquid contained 0.01 N sodium chloride, the pH being adjusted by the addition of suitable amounts of hydrochloric acid, or above pH 6 by caustic soda. Because of the dependence of the mobility on pH the dispersion and supernatant liquid must be matched as regards pH . Above pH 7 it was found necessary to employ a buffer, sodium diborate, in order to ensure satisfactory matching of the pH values of the dispersion and supernatant liquid. In order to obtain clear boundaries the dispersion must have a greater density than the supernatant liquid. In every case, therefore, the dispersion contained 2 % of A.R. sucrose. Northrop and Cullen²

² Northrop and Cullen, *Journ. Gen. Physiol.*, 1922, 4, 635.

have shown that this small amount of sugar has a negligible effect on the electrophoretic mobility.

Results.

Complete mobility- pH curves have been obtained for a number of emulsions in which the stearic acid concentration in ethyl laurate is varied

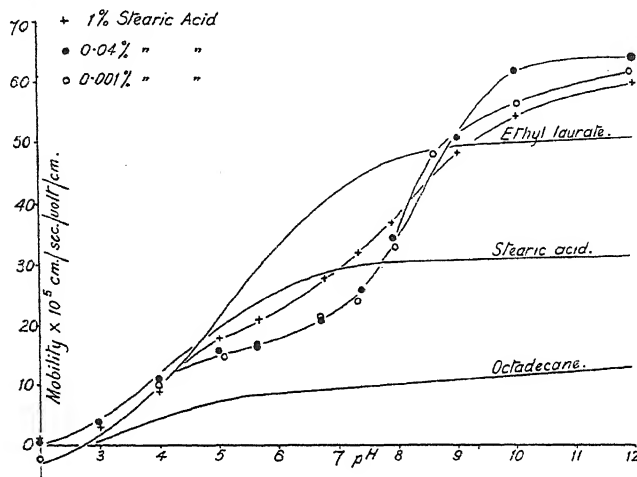


FIG. 1.—The mobility of droplets of ethyl laurate containing various amounts of stearic acid.

as far as is permitted by the relatively limited solubility of the acid in this ester. To illustrate the general behaviour a few curves are given in Fig. 1 in which mobility is plotted as a function of pH of the medium. For the sake of comparison the curves for ethyl laurate and for stearic acid obtained by Carruthers³ and Roberts⁴ (and confirmed by the writer) are shown in Fig. 1, as is also the curve for octadecane obtained by Williams.⁵

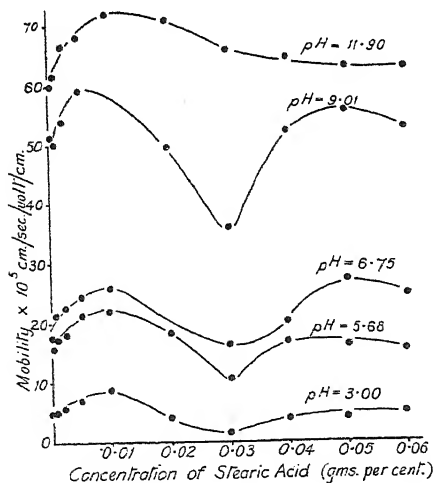


FIG. 2.—Mobility of droplets of ethyl laurate containing various concentrations of stearic acid.

In the region of high stearic acid content, e.g., when 1 % of stearic is present—a quantity which exceeds the ordinary solubility of the acid in this ester—the mobility in the very alkaline region ($pH = 11.9$) is high compared with that exhibited by the pure acid itself. This unexpected result which is obtained (and apparently confirmed by careful repetition) likewise at $pH 9$ is not ob-

³ Carruthers, *Trans. Faraday Soc.*, 1938, 34, 300.

⁴ Roberts, Ph.D. Thesis, Liverpool (1937).

⁵ Williams, Ph.D. Thesis, Liverpool (1940).

tained at lower pH values at which the mobility of the droplet containing 1 % stearic acid approximates to the value for the pure acid particle itself.

Perhaps the effect of the presence of stearic acid in the ester droplets is most clearly shown in Fig. 2 in which mobility is plotted against composition of droplet at a series of pH values. It can be asserted with some confidence that a maximum in the mobility- pH curve manifests itself in the region of 0.01 % stearic in ester. There also appears to be a second maximum in the neighbourhood of 0.05 % stearic acid with a minimum at 0.03 %. It is impossible to suggest at the present stage an adequate explanation for the very complex behaviour illustrated in Fig. 2.

Effect of Time on the Mobility in the Alkaline Region.—Above pH 9 there is the possibility that stearic acid may be dissolved out of the droplets to form soap. It might be expected that the magnitude of this effect would change with time. To see if this is the case droplets of ethyl laurate containing 0.06 % of stearic acid were placed in contact with 0.01 N caustic soda and their mobility determined. After five hours, the mobility was again determined.

pH —11.90.

Mobility initially 64.8×10^{-5}

Mobility on standing 64.3×10^{-5} cm./sec./volt/cm.

A similar experiment was carried out with droplets of stearic acid.

pH —11.90.

Mobility initially 33.0×10^{-5}

Mobility on standing 32.2×10^{-5} cm./sec./volt/cm.

These results indicate that the mobilities of the droplets do not change with time.

Discussion of Results.

On emulsifying the mixtures it may be concluded that some of the stearic acid will be present at the ethyl laurate water interface. There are reasonable grounds also for thinking that at the interface the $-\text{COOH}$ groups of the fatty acids are oriented towards the water, as are also the $-\text{COOET}$ groups of the ester.

On general grounds it would be expected that the pH -mobility curve for composite droplets of ethyl laurate and stearic acid should lie between the curves for the separate components and as the concentration of stearic acid increases the shape of the pH -mobility curve of the composite droplets should approach that of pure stearic acid. This, however, is not the case, as is shown in Figs. 1 and 2. The results show, therefore, that a stearic acid molecule at the surface of an ethyl laurate droplet does not act in the same manner as that at the surface of a pure stearic acid particle.

It would be premature to speculate upon the reasons for this until further work has been carried out on similar systems.

Summary.

The electrophoretic mobilities of droplets of esters containing various amounts of stearic acid have been determined in the presence of 0.01 N sodium ion over the range pH 2 to 12.

The mobilities observed for these composite droplets do not lie in an intermediate position with respect to the mobilities of the two constituents by themselves. It is inferred that the orientation of the surface layer of the stearic acid in the composite droplet differs from that which occurs in the case of particles of stearic acid itself.

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SOME ANOMALIES BETWEEN ELECTROPHORETIC MOBILITY AND INTERFACIAL TENSION DATA FOR PARAFFIN CHAIN SALT SOLUTIONS.

BY J. POWNEY AND L. J. WOOD.

Received 23rd December, 1940.

It is the purpose of this short paper to describe some measurements we have recently made of the electrophoretic mobilities of oil drops in paraffin chain salt solutions, together with interfacial tension data for the same systems. If both the electrophoretic mobility and the lowering of interfacial tension depend on the formation of interfacial films some qualitative agreement might be anticipated between the two sets of data. In a number of instances, however, the change in electrophoretic mobility with concentration appears to bear no relationship to the change in interfacial tension, and this is particularly marked at the lower concentrations where we have frequently observed high mobility maxima in solutions which exhibit inappreciable interfacial activity. These high mobilities can arise only from the influence of the long chain ions, and it is hoped that the data now given may invoke discussion as to the location and orientation of such ions at the oil-water interface under these conditions.

Experimental.

For the determination of electrophoretic mobilities a cell based on the same principle as that used by Smith and Lisse¹ was employed. The method of operation, preparation of Nujol emulsions, and general precautions observed have been described in previous publications.² A stock oleic acid-water emulsion was prepared by means of a mechanical emulsifier using Kahlbaum "oleic acid purest". The interfacial tension data were obtained by a drop-pipette method as previously described.³ It has been found convenient to compare mobility measurements of Nujol (liquid paraffin) with interfacial tensions of xylene, but this difference in the oil used for the two sets of data does not invalidate comparison. For all experiments water of conductivity 2×10^{-6} ohm.⁻¹ cm.⁻¹ was used.

Results and Discussion.

The Interface "Oil/Dodecyl Pyridinium Iodide Solution".

Perhaps the most outstanding anomaly between electrophoretic mobility and interfacial tension data is that shown in the system oil dodecyl pyridinium iodide (see Fig. 1, curves A, A'). Whilst the mobility of Nujol in water is $-4.35 \mu/\text{sec.}/\text{volt}/\text{cm.}$ at 25° , the addition of only 0.000075 % $\text{C}_{12}\text{H}_{25} \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{I}$ reduces the mobility to zero and on further increasing the concentration to 0.0004 % the mobility attains a maximum value of $+5.8$. Similar changes in mobility have also been observed in

¹ Smith and Lisse, *J. Physic. Chem.*, 1936, 40, 399.

² Powney and Wood, *Trans. Faraday Soc.*, 1940, 36, 57, 420.

³ Powney and Addison, *ibid.*, 1937, 33, 1243.

$C_{12}H_{25} \cdot C_5H_5N \cdot Cl$ solutions.² Lowering of interfacial tension, on the other hand, is quite inappreciable at concentrations below 0.01 % and it is only when the critical concentration (approximately 0.4 %) is reached that the mobility and interfacial tension data show any correlation. The high positive mobility shown at extremely low concentrations can only be due to the dodecyl pyridinium cations and the question arises as to whether these long chains will be situated actually in the oil-water interface, a process which might be favoured by the strong electrostatic attraction, or be present as an atmosphere in proximity to the interface. If there is definite adsorption, then it is difficult to understand why there should be no measurable interfacial activity even at concentrations twenty times higher than those at which high positive mobilities are attained. On the other hand, if there is no adsorbed film in the normal sense of the term, it is difficult to reconcile the incomparably greater sensitivity of the mobility of Nujol towards $C_{12}H_{25} \cdot C_5H_5N \cdot I$ than towards a simple univalent electrolyte such as $NaCl$.²

The Interface "Oil/Anion-active Salt Solution".

The electrophoretic behaviour described in the previous paragraph is also shown to some extent in dilute solutions of anion-active paraffin

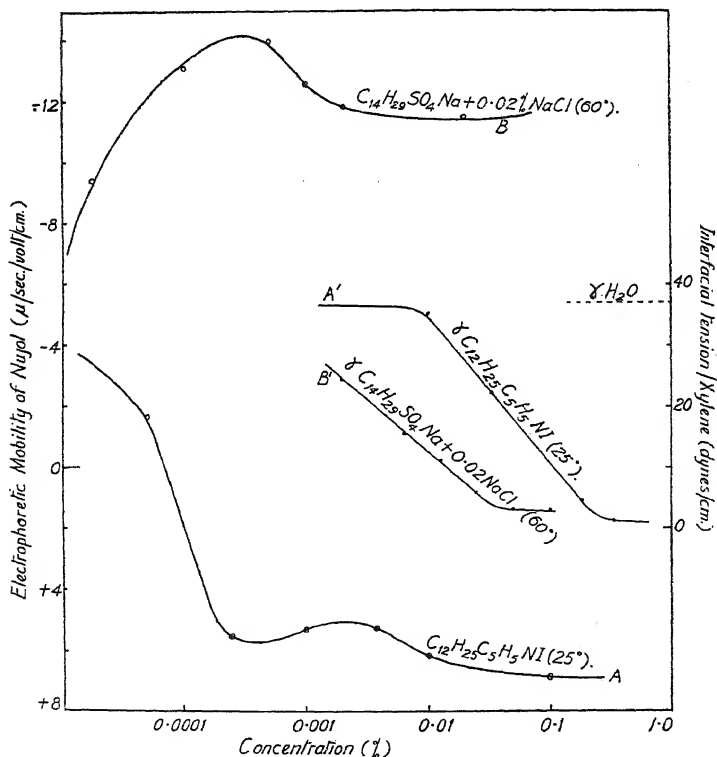


FIG. 1.—Electrophoretic mobility and interfacial tension data for dodecyl pyridinium iodide and sodium tetradecyl sulphate solutions.

chain salts such as sodium dodecyl sulphate, sodium tetradecyl sulphate and sodium laurate. The mobility of Nujol in dilute solutions of sodium

tetradecyl sulphate containing 0.02 % added NaCl shows large changes at concentrations well below those at which there is any appreciable interfacial activity (see Fig. 1, curves B, B'). In this instance the measure-

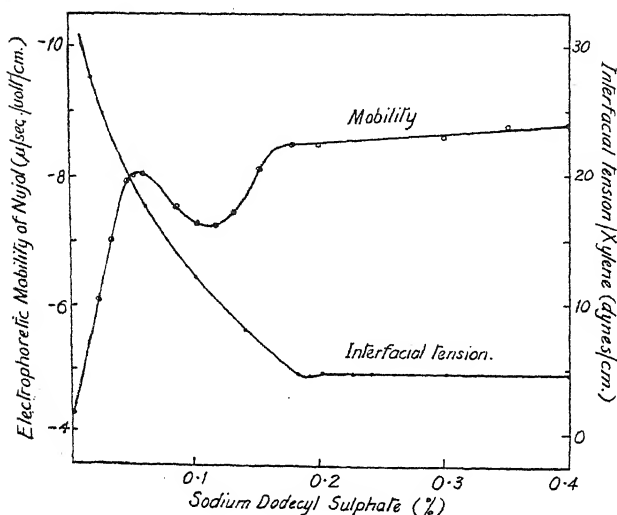


FIG. 2.—Electrophoretic mobility and interfacial tension data for sodium dodecyl sulphate solutions (25°).

ments were made at 60°, the mobility of Nujol at this temperature being approximately $-5 \mu/\text{sec.}/\text{volt}/\text{cm.}$ in 0.02 % NaCl and -8.3 in pure water. At a concentration of only 0.0005 % $\text{C}_{14}\text{H}_{29}\text{SO}_4\text{Na}$ the remarkably high mobility of -14 is reached.

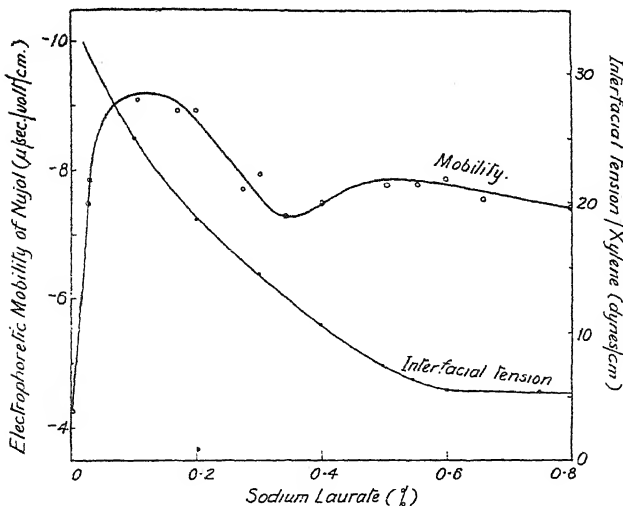


FIG. 3.—Electrophoretic mobility and interfacial tension data for sodium laurate solutions (25°).

The data for sodium dodecyl sulphate and sodium laurate are given in Figs. 2 and 3. In both cases the maximum mobility occurs at concentrations at which there is only a small lowering of interfacial tension.

The Interface "Oleic Acid/Sodium Oleate Solution".

In a previous investigation,⁴ it was found that the interfacial tension of oleic acid was not appreciably lowered by even quite high concentrations of sodium oleate (e.g. 0.7 % sodium oleate only reduces the tension by one dyne) and it was thought of interest to determine electrophoretic mobilities in this system (Fig. 4). The low interfacial activity of sodium

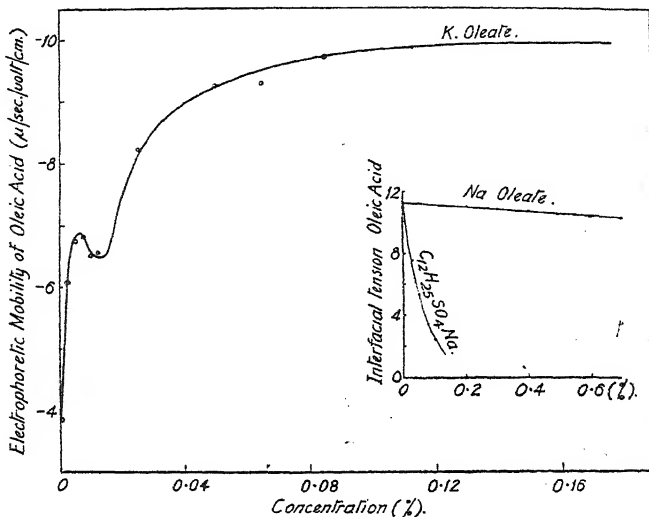


FIG. 4.—Electrophoretic mobility and interfacial tension data for oleic acid (20°).

oleate in this case is presumably due to the *pH* gradient at the interface preventing the adsorption of sodium oleate since unhydrolysed paraffin chain salts such as sodium dodecyl sulphate cause a very considerable lowering of the interfacial tension of oleic acid. As far as mobility is concerned the *pH* gradient appears to have no restricting influence on potassium oleate,* which causes changes in the mobility of oleic acid (Fig. 4) comparable with those found for oleic acid in sodium tetradecyl sulphate solutions. In this instance, at least, it must be assumed that the long chain oleate ions can influence the mobility without being actually present in the interface.

Summary.

Measurements of electrophoretic mobilities of oil drops in paraffin chain salt solutions are compared with interfacial tension data for corresponding oil-paraffin chain salt solution interfaces. Several instances are recorded of high mobilities due to surface-active ions under conditions which give rise to little or no lowering of interfacial tension.

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⁴ Powney and Addison, *Trans. Faraday Soc.*, 1938, 34, 628.

* Although potassium oleate was used, there is no reason to suppose that sodium oleate would have behaved otherwise.

THE EFFECT OF SALTS ON SOLUBLE IONISED MONOLAYERS.

BY A. B. D. CASSIE AND R. C. PALMER.

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Only ionised monolayers are strongly affected by salts: Pankratov,¹ for example, has found that potassium and calcium chlorides and other salts have no large effect on films of cetyl alcohol or esters; and it is well known that fatty acids on a substrate of $pH\ 2$ are unaffected. The behaviour of ionised monolayers towards salts is strongly dependent on the ions of opposite sign to those of the film, but differs according as the film is a strong or weak electrolyte. The effect of traces of polyvalent cations on films of, for example, fatty acids has been discussed by several workers,^{2, 3, 4, 5, 6} and has been treated successfully by means of a modified Langmuir adsorption isotherm by Langmuir and Schaefer.⁷ The main action of salts on these films is to give an increase in rigidity and an alteration in surface potential. Weak electrolyte films are not discussed in the present paper.

On strong electrolyte films the effect of salts is different: there is, for example, no pronounced action on the mechanical properties of insoluble strong electrolyte films.⁸ Salts, and again particularly the ions of charge opposite to the film, alter the distribution of a soluble capillary active substance between the bulk and the surface, which manifests itself as a lowering of surface or interfacial tension. There is a good deal of evidence of increased capillary activity of paraffin chain salts below the critical concentration for micelles in the presence of electrolytes at an air-water,^{9, 10} oil-water,¹¹⁻¹⁴ or solid hydrophobic interface; ¹⁵ the effect of salts in increasing the detergent power of soap ¹⁶ and other detergents ¹⁷ is also evidence of the increased capillary activity.

The effect of salts on strong electrolyte films has been discussed mathematically by Muto,¹⁸ who finds that the effect is a symmetrical function of the ionic content of the solution; whereas in fact it is characteristic of these phenomena that they are almost entirely dependent on

¹ Pankratov, *Acta Physicochim. U.R.S.S.*, 1939, **10**, 45.

² Harkins and Myers, 1937, *Nature*, **139**, 367.

³ Mitchell, Rideal, and Schulman, 1937, *ibid.*, **136**, 625.

⁴ Gerovick and Vargin, 1937, *Bull. Acad. Sci. U.R.S.S., Class Sci. Math. Nat., Series Chem.*, 1075.

⁵ Langmuir and Schaefer, *J. Amer. Chem. Soc.*, 1937, **59**, 2400.

⁶ Trapeznikov, *Acta Physicochim. U.R.S.S.*, 1939, **10**, 65.

⁷ Langmuir and Schaefer, *J. Amer. Chem. Soc.*, 1937, **58**, 284.

⁸ Stenhagen, *Trans. Faraday Soc.*, 1940, **36**, 496.

⁹ Long, Nutting, and Harkins, *J. Amer. Chem. Soc.*, 1937, **59**, 2197.

¹⁰ Powney and Addison, *Trans. Faraday Soc.*, 1937, **33**, 1253.

¹¹ Harkins and Zollman, *J. Amer. Chem. Soc.*, 1926, **48**, 69.

¹² Robinson, *Nature*, 1937, **139**, 626.

¹³ Adam, *J. Soc. Dyers Col.*, 1937, **53**, 121.

¹⁴ Boutaric and Breton, *Bull. Soc. Chim.*, 1937, 1793.

¹⁵ Palmer and Rideal, *J. Chem. Soc.*, 1939, 573.

¹⁶ Rhodes and Wynne, *Ind. Eng. Chem.*, 1937, **29**, 55.

¹⁷ Palmer, *J. S. C. I.*, *in the press*.

¹⁸ Muto, *Proc. Phys.-Math. Soc. Japan*, 1938, **20**, 646.

the ions of opposite sign to the surface active species. The theory developed in this paper shows that the effect of salts can be successfully treated by considering the effect of the redistribution of ions under the film in altering the potential energy of the molecules in the film, and so altering the adsorption of capillary active molecules from solution.

1. Working Hypotheses and Assumptions of the Theory.

1. Non-electrolyte molecules that are positively adsorbed at an interface will lose on passing from the bulk to the interface an amount of potential energy that depends on the properties of the molecule and the two phases forming the interface; hence, applying the Boltzmann principle, the distribution of the molecules in the bulk and in the interface is given by

$$\frac{c_s}{c} = e^{\frac{\omega}{kT}} \quad (1)$$

where c is the bulk concentration in molecules per c.c. and ω is the decrease in potential energy of the system when a molecule passes from the bulk to the interface; c_s measures the surface concentration, and has the dimensions of number per c.c., but it cannot be easily interpreted. It will be primarily a function of Γ , the ordinary thermodynamic surface excess expressed as number per sq. cm. The first assumption of the present theory is that it is a function of Γ only, *i.e.*,

$$c_s = c_s(\Gamma) \quad (2)$$

2. A second simplifying assumption is that a constant surface pressure implies a constant surface excess, or that for one surface active ion at one interface, the surface pressure is a function of Γ alone, and is dependent on the ionic distribution below the surface film only through Γ .

3. If ions are positively adsorbed, they will give effectively a plane charge at the interface, and the decrease in potential energy of the system when an ion of the same sign passes from the bulk to the surface will be greatly diminished. If the potential in the neighbourhood of the ionised groups of the molecules is ϕ in the film and ϕ' in the solution, the change in electrical energy on passing from the bulk to the surface is $ze(\phi - \phi')$. The third hypothesis is that the non-electrical energy, ω , and the electrical energy are additive; *i.e.*, for an ionised surface active species equation (1) becomes

$$\frac{c_s}{c} = e^{(\omega - ze\phi - \phi')/kT} \quad (3)$$

If the surface were uniformly charged with no ions of opposite sign concentrated near it, ϕ would be infinite, and no ions would reach the surface. The presence of a concentration of ions of opposite sign does, however, make ϕ finite, though very sensitive to changes in the ions of opposite sign to those adsorbed at the surface. The potential ϕ' is that due to the ion atmosphere in solution and considered in Debye-Hückel theory. The term containing ϕ' may, therefore, be removed if we replace the concentration c by the activity. Equation (3) thus becomes:

$$\frac{c_s}{\gamma c} = e^{(\omega - ze\phi)/kT} \quad (4)$$

where γ is the activity coefficient of the detergent ions.

4. The fourth hypothesis concerns the value of ω . The theory presented here is intended to cover films from moderate pressures up to 30 dynes/cm. or more; and although the molecules in these films will not be lying flat at the interface, it is assumed that $\Delta\omega$, the increase in ω for one CH_2 group, is approximately constant from 12 to 18 carbon atoms. It is further assumed that $n\Delta\omega$ (where n is the number of CH_2 groups in the chain) will give a rough measure of ω . Equations (1) and (2) applied to data given by Powney and Addison¹⁹ for sodium dodecyl sulphate to sodium octadecyl sulphate adsorbed at a water-xylene interface show $\Delta\omega$ to be roughly $0.85 kT$. Thus for the films discussed here, 12 to 18 carbon atoms, ω will be of the order of $12 kT$.

2. Properties of Surface Active Ions with Added Salt in Solution.

If electrical effects are to influence the extent of adsorption, $\epsilon\phi$ must be of the order of ω , or at least $5kT$. This value for $\epsilon\phi$ rules out the ordinary Debye-Hückel approximations where it is assumed that $\epsilon\phi/kT \ll 1$. For the special case, however, of a plane uniformity charged surface in contact with a solution of strong electrolytes, the Poisson-Boltzmann equation can be integrated without making this approximation. This equation is²⁰:

$$\frac{d^2\phi}{dx^2} = -\frac{4\pi}{D} \sum z_i n_i \epsilon e^{-z_i \epsilon\phi/kT} \quad . \quad . \quad . \quad (5)$$

where x is the direction normal to the surface, D is the dielectric constant, and z_i is the valency of ions of number n_i per c.c. in the bulk of the solution, including c . Equation (5) can be immediately integrated to give for the boundary conditions:

$$x = \infty : \phi = 0 : \frac{d\phi}{dx} = 0,$$

$$\frac{1}{2} \left(\frac{d\phi}{dx} \right)^2 = \frac{4\pi kT}{D} \sum n_i (e^{-z_i \epsilon\phi/kT} - 1) \quad . \quad . \quad . \quad (6)$$

If the surface of adsorbed ions is replaced by a plane surface of uniform charge σ per unit area,

$$\left(\frac{d\phi}{dx} \right)_{x=0} = -\frac{4\pi\sigma}{D} \quad . \quad . \quad . \quad (7)$$

and

$$\sigma^2 = \frac{DkT}{2\pi} \sum n_i (e^{-z_i \epsilon\phi/kT} - 1) \quad . \quad . \quad . \quad (8)$$

The convention used in deducing (5) is that approach of ions of the same sign increases the energy of the system: hence σ and ϕ have the same sign in equation (8). If, as will be usual in the present paper, anions are adsorbed at the surface, ϕ will be negative, and $-z_i \epsilon\phi$ will be positive for cations, and negative for anions. As pointed out above, $\epsilon\phi$ must be of the order of $5 kT$, so for monovalent cations $e^{-z_i \epsilon\phi/kT}$ becomes $e^{|\epsilon\phi/kT|}$, or is of the order of 10^2 or more; similarly, the contribution of the anions in solution to the R.H.S. of (8) is less than 10^{-2} , and can be

¹⁹ Powney and Addison, *Trans. Faraday Soc.*, 1937, **33**, 1243.

²⁰ Müller, *Cold Spring Harbor Symposia on Quantitative Biology*, 1933, **1**, 3.

wholly neglected. The effect of salts on films of long chain anions will, therefore, be independent of the nature of the anion in solution. This agrees with Robinson's¹² and Palmer's¹⁷ experimental observations. One notes that the term (-1) on the R.H.S. of (8) will also, in general, be negligible compared with $e^{12e\phi/kT}$ and a good approximation for (8) is:

$$\sigma^2 = \frac{DkT}{2\pi} \left\{ n_1 e^{1e\phi/kT} + n_2 e^{12e\phi/kT} + \dots \right\} \quad (9)$$

where n_1, n_2, \dots are the numbers of ions per c.c. of solution of opposite sign to σ , and of valency 1, 2, \dots

Equation (9) is a simple formula, but it cannot be tested against experimental results until some interpretation has been given for σ . Clearly, σ cannot be identified with the surface excess of ions, Γ , multiplied by their charge, because equation (7) depends on the field of force normal to the plane. When the uniform charge is replaced by point charges in the plane, $\left(\frac{d\phi}{dx}\right)$, the component of the electric field in the x direction, will be equal to or less than the field in its resultant direction. Replacement of the uniformly charged surface by point charges will also influence the distribution of ions under the surface, and $\left(\frac{d\phi}{dx}\right)$ will depend to a secondary extent on these ions. As a first approximation, however, σ may be taken as a function of Γ alone: *i.e.*,

$$\sigma = \sigma(\Gamma) \quad (10)$$

Equations (2), (4), (9) and (10) can be used to explain many of the observed effects of salts on the interfacial tensions of strong electrolyte detergents. Consider two solutions having the same interfacial tension against a certain liquid and containing (i) detergent alone, and (ii) detergent with added salt. If the interfacial tension is fixed, Γ is fixed, and, therefore, c_s and σ are constants. If r be the valency of the cation of the added salt, equation (8) gives:

$$c_r e^{1e\phi/kT} + n_r e^{1re\phi/kT} = \frac{2\pi\sigma^2}{DkT} \quad (11)$$

where c_r is the concentration of detergent, and n_r is that of the cation, both in molecules per c.c., which together give an interfacial tension equivalent to σ . The factors $e^{1e\phi/kT}$ and $e^{1re\phi/kT}$ can be replaced from equation (4), which is now:

$$\frac{\gamma_r c_r}{c_s} = e^{1e\phi/kT} e^{-\omega/kT} \quad (12)$$

The substitution gives:

$$\gamma_r c_r \left[c_r + n_r \left(\frac{\gamma_r c_r}{c_s} \right)^{r-1} e^{(r-1)\omega/kT} \right] = \frac{2\pi\sigma^2}{DkT} c_s e^{-\omega/kT} \quad (13)$$

Equations (2) and (10) show the R.H.S. of (13) to be constant when one value of interfacial tension is used. Writing

$$c_s e^{-\omega/kT} = \mu \quad (14)$$

and

$$\frac{2\pi\sigma^2}{DkT} c_s e^{-\omega/kT} = \lambda^2 \quad (15)$$

equation (13) gives :

(i) for no added salt,

$$\gamma_0 c_0^2 = \lambda^2 \quad . \quad . \quad . \quad (16.0)$$

(ii) for added uni-valent cation salt,

$$\gamma_1 c_1 (c_1 + n_1) = \lambda^2 \quad . \quad . \quad . \quad (16.1)$$

(iii) for added di-valent cation salt,

$$\gamma_2 c_2^2 \left(1 + n_2 \frac{\gamma_2}{\mu} \right) = \lambda^2 \quad . \quad . \quad . \quad (16.2)$$

(iv) for added tri-valent cation salt,

$$\gamma_3 c_3^2 \left(1 + n_3 \frac{\gamma_3^2 c_3}{\mu^2} \right) = \lambda^2 \quad . \quad . \quad . \quad (16.3)$$

(r) for added r-valent cation salt,

$$\gamma_r c_r^2 \left(1 + n_r \frac{\gamma_r^{r-1} c_r^{r-2}}{\mu^{r-1}} \right) = \lambda^2 \quad . \quad . \quad (16.r)$$

Comparison with Experimental Observations.

Formulae (16.0) to (16.3) can be tested by available experimental data. Powney and Addison¹⁰ give data for the interfacial tension between an aqueous solution of sodium dodecyl sulphate and xylene at 20° C. when various amounts of NaCl are added to the aqueous phase. Their data give the concentrations of detergent, [S], and of NaCl that give an interfacial tension of 5.5 dynes/cm. Equations (16.0) and (16.1) show that for this case :

$$\gamma_1 [S] ([S] + [\text{NaCl}]) = \lambda^2 \quad . \quad . \quad . \quad (17)$$

where λ is here measured in moles per litre. Equation (17) covers both zero and finite concentrations of NaCl. Table I gives Powney and Addison's data, together with the product of equation (17). The activity coefficients were calculated, using the equation :

$$-\log_{10} \gamma = 0.5 \sqrt{\sum_i c_i z_i^2} \quad . \quad . \quad . \quad (18)$$

The values of γ given can only be regarded as approximate because the peculiar shape of the detergent ions will invalidate to some extent the derivation of equation (18); but as the activity coefficient correction is small, this is unimportant.

TABLE I.

[S].	[NaCl].	γ_1 .	$\gamma_1 [S] ([S] + [\text{NaCl}]) = \lambda^2$.
6.0×10^{-3}	0.0×10^{-3}	0.915	33×10^{-6}
4.6×10^{-3}	4.3×10^{-3}	0.896	37×10^{-6}
2.4×10^{-3}	17.0×10^{-3}	0.851	40×10^{-6}
1.6×10^{-3}	34.0×10^{-3}	0.805	46×10^{-6}
0.4×10^{-3}	170.0×10^{-3}	0.622*	42×10^{-6}

* This activity coefficient is probably a good deal too low because equation (18) does not hold for such a high salt concentration as 0.17 M.

increasing salt concentration. This must, however, be expected, because the dielectric constant of an ionic solution is less than that of water in bulk on account of the electric saturation around each ion.²¹ There will,

In considering the constancy of the last column in Table I, the large range both of salt and detergent concentration should be noted. The last column shows an increase with

therefore, be a decrease in D and an increase in λ (see equation (15)) with increasing salt concentration. The effective surface density of charge, σ , will also vary with salt concentration, but the near constancy of the last column in Table I shows that the assumption of equation (10) is justified.

Powney and Addison also give data for addition of CaCl_2 to sodium dodecyl sulphate. The data for NaCl and CaCl_2 can be used to test equations (16.1) and (16.2). If c_2 is taken equal to c_1 , any given interfacial tension can be obtained by varying n_1 and n_2 . When

$$c_1 = c_2 = c \quad (19)$$

equations (16.1) and (16.2) give

$$\frac{\gamma_2 n_2}{\gamma_1 - \gamma_2 + \frac{\gamma_1 n_1}{\gamma_2 c}} = \mu \quad (20)$$

where μ depends on interfacial tension only. The activity coefficient is found to be negligible in this case with the data used; so putting γ_1 and γ_2 both equal to unity, (20) becomes

$$\frac{n_2 c}{n_1} = \mu \quad (21)$$

Table II gives appropriate data from Powney and Addison's paper for interfacial tensions of 5.5 and 7 dynes/cm., together with the product $[\text{Ca}][\text{S}]/[\text{Na}]$.

TABLE II.

Interfacial Tension (Dynes per cm.).	Detergent conc. [S].	[Na].	[Ca].	$\frac{[\text{Ca}][\text{S}]}{[\text{Na}]} = \mu$.
7.0	5.0×10^{-3}	1.37×10^{-3}	0.40×10^{-5}	1.5×10^{-5}
7.0	4.0×10^{-3}	3.72×10^{-3}	1.98×10^{-5}	2.1×10^{-5}
7.0	3.0×10^{-3}	8.10×10^{-3}	4.47×10^{-5}	1.7×10^{-5}
7.0	2.1×10^{-3}	14.9×10^{-3}	9.0×10^{-5}	1.3×10^{-5}
5.5	5.0×10^{-3}	3.03×10^{-3}	1.25×10^{-5}	2.05×10^{-5}
5.5	4.0×10^{-3}	5.91×10^{-3}	3.17×10^{-5}	2.1×10^{-5}
5.5	3.0×10^{-3}	10.1×10^{-3}	6.2×10^{-5}	1.9×10^{-5}
5.5	2.4×10^{-3}	16.2×10^{-3}	9.1×10^{-5}	1.4×10^{-5}

The last column should be constant. It shows irregular variations, which are probably due to the difficulty of interpolating accurate values for $[\text{Na}]$ and $[\text{Ca}]$ from Powney and Addison's graphs. It should be noted that μ is independent of D and σ , and so should not be subject to the factors that make λ vary in Table I. The constancy of μ verifies equation (16.2).

Equation (16.3) can be checked from data given by Robinson.¹² He states that with 0.005 % $\text{C}_{17}\text{H}_{33}\text{CON}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$, the concentration of salt required to diminish a water-oil interfacial tension from 6.25 to 1.0 dynes/cm. was 0.32 N NaCl , 0.003 N CaCl_2 , and 5×10^{-5} N LaCl_3 . Here c_1 , c_2 , and c_3 have the constant value 1.16×10^{-4} M. This means that λ and μ can be eliminated from equations (16.1) (16.2) and (16.3). Neglecting c in comparison with n_1 , the result is:

$$n_3 = \frac{\gamma_2^4 n_2^2}{\gamma_3^3 \gamma_1 n_1} \quad (22)$$

If Robinson's values for $[\text{CaCl}_2]$ and $[\text{NaCl}]$ and estimates of the activity coefficients from equation (18) are inserted in equation (22), the concentration of LaCl_3 required to give the interfacial tension of 1.0 dynes/cm.

is 3.0×10^{-5} N. This estimate is reasonably close to the observed concentration of 5×10^{-5} N, considering the uncertainty in γ_1 , for so strong a solution. (Note that if all the γ 's are taken as unity n_3 is hardly affected, being 2.5×10^{-5} N.)

Traces of Cations of Higher Valencies and Surface Active Electrolytes.

Robinson²² has drawn attention to the large effect on strong electrolyte films of traces of polyvalent metallic ions in the solution. It is worth noting that the present theory predicts such effects. An example was given in the last section where Robinson's data on the effect of traces of LaCl_3 on interfacial tension was semi-quantitatively explained. A large surface effect is always to be expected with strong electrolyte detergents; for equations (13) and (16) show that the cation concentration required for any given interfacial tension is always divided by μ^{r-1} in these formulæ; as μ is less than 10^{-5} M for surface active ions, the value of n_r required to influence surface properties becomes very small as r increases.

It is obvious from equation (16·r) that polyvalent ion effects will be most noticeable in solutions with no other added salts. This equation shows that if the polyvalent ions are to introduce appreciable effects, say 10 %, then

$$\frac{n_r}{\mu^{r-1}} c_s^{r-2} \approx 10^{-1} \quad . \quad . \quad . \quad (23)$$

which may be written in the form :

$$n_r = 10^{-1} c_s^{r-1} e^{-\omega/kT} \left(\frac{e^{-\omega/kT}}{c} \right)^{r-2} \quad . \quad . \quad (24)$$

It has been assumed in section 1 that $e^{-\omega/kT}/c$ is approximately constant for a constant interfacial tension given by a homologous series between 12 and 18 carbon atoms. Hence, the amount of any polyvalent cation necessary to give appreciable effects is directly proportional to $e^{-\omega/kT}$. Take the case of sodium dodecyl sulphate, where for an interfacial tension lowering of 30 dynes/cm. with water and xylene, c is roughly 6×10^{-3} , and μ is roughly 2×10^{-5} M.

Equation (23) gives :

$$\begin{array}{ll} \text{(i) for } r = 3 & n_3 = 6 \times 10^{-9} \text{ M,} \\ \text{and} & \\ \text{(ii) for } r = 4 & n_4 = 2 \times 10^{-11} \text{ M.} \end{array}$$

The factor $e^{-\omega/kT}$ diminishes twofold for every CH_2 group added to the chain (see section 1), and c_s will be roughly independent of chain length. Hence for sodium octadecyl sulphate, appreciable changes of interfacial tension will occur when trivalent cations are present in an amount 3×10^{-11} M, and when quadrivalent ions are present as 10^{-13} M.

3. Miscellaneous Applications of the Theory.

Surface Equations of State for Strong Electrolyte Detergents.

The theory of the preceding paragraphs has readily explained available experimental data on the effect of salts on interfacial tensions of surface active strong electrolytes. A necessary condition for the theory to be valid is that it should lead to a reasonable surface equation of state for the surface active materials. If σ were a known function of Γ ,

²² Robinson, *Symposium on Wetting and Detergency*, A. Harvey Ltd., 1937, 137, 150.

the theory would lead at once to an equation of state. This function is unknown at present, but it will be shown below that the theory leads to a criterion that must be satisfied by any equation of state.

Suppose that the surface active material is a non-electrolyte and the surface equation of state is :

$$F = f_n(A) \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where F is the surface pressure when the molecule occupies an area A . Gibbs's equation for a single solute can be written :

$$\frac{1}{A} = \frac{1}{RT} \frac{dF}{d(\log c)} = \frac{1}{RT} \frac{dF}{dA} \frac{dA}{d(\log c)} \quad . \quad . \quad (26)$$

Substitution for $\frac{dF}{dA}$ from (25) in (26), and integration of (26) gives :

$$\log c = \frac{Af_n(A)}{RT} - \int \frac{f_n(A)}{RT} dA + \text{const.} \quad . \quad . \quad (27)$$

It has been shown in section 1 that if F , and therefore A , is constant, c decreases by a constant factor for every CH_2 group added to the chain of a homologous series. The constant in (27) must, therefore, contain the term $-\omega/kT$, where ω is the energy gained by the system when one molecule of the surface active material passes from the bulk of the solution to the interface. (27) may thus be written :

$$\log c = \frac{Af_n(A)}{RT} - \int \frac{f_n(A)}{RT} dA - \frac{\omega}{kT} + \alpha \quad . \quad . \quad (28)$$

where α is a constant.

When a uni-valent surface active electrolyte is the solute, ω is decreased by an amount $\epsilon\phi$, and (28) becomes

$$\log c = \frac{Af_n(A)}{RT} - \int \frac{f_n(A)}{RT} dA - \frac{\omega - \epsilon\phi}{kT} + \alpha \quad . \quad (29)$$

The electrical equation (9) for this case is :

$$\log c = 2 \log \sigma - \frac{\epsilon\phi}{kT} + \log \frac{2\pi}{DkT} \quad . \quad . \quad (30)$$

Addition of (29) and (30) gives :

$$2 \log c = \frac{Af_n(A)}{RT} - \int \frac{f_n(A)}{RT} dA + 2 \log \sigma(A) + \beta \quad . \quad (31)$$

where β is a constant for any one surface active material. σ may, to a first approximation, be taken as dependent only on A , and as a function of c only through A , (Equation (10)).

Equation (31) must obey Gibbs's equation for a single solute if each anion and a corresponding cation be taken as a single species. This can always be done, for the solution and interface are, as a whole, electrically neutral. Differentiating (31) and substituting in Gibbs's equation, (26), gives :

$$2 \frac{dF_e}{dA} = f_n'(A) + \frac{2RT}{\sigma A} \frac{d\sigma}{dA} \quad . \quad . \quad (32)$$

where F_e is the surface pressure for the electrolyte case, and f_n is the surface pressure for the non-electrolyte case.

Experimental data suitable for testing this equation are sparse. However, if an equation of the form

$$(F - F_0)(A - A_0) = xRT \quad . \quad . \quad . \quad (33)$$

is assumed for an ionised film at a benzene-water interface, with $x = 1$ for the same film when unionised, equation (32) leads to a value of $x = 3/2$, when A is much greater than A_0 . This result is arrived at in the following way. Equation (33) may be written:

$$F = F_0 + \frac{RT}{A - A_0} + \frac{(x - 1)RT}{A - A_0} \quad . \quad . \quad . \quad (33a)$$

which, when $A \gg A_0$, may be written:

$$F = F_0 + \frac{RT}{A - A_0} + \frac{(x - 1)RT}{A} \quad . \quad . \quad . \quad (33b)$$

Substituting for $f_n'(A)$ from (33b) ($x = 1$) and for $\frac{dF_e}{dA}$ from (33b) ($x = x$) in (32), the differential equation for σ is found to be:

$$\frac{2}{\sigma} \frac{d\sigma}{dA} + \frac{A}{(A - A_0)^2} + \frac{2(x - 1)}{A} = 0 \quad . \quad . \quad . \quad (34)$$

or

$$\sigma^2(A - A_0)A^{2(x-1)} = \kappa e^{A_0/(A - A_0)} \quad . \quad . \quad . \quad (35)$$

where κ is the integration constant. If (35) is to give σ varying as $1/A$ when A is large, $x - 1$ must be $\frac{1}{2}$, i.e. x must be 1.5.

The only direct experimental evidence available appears to be that of Alexander and Teorell,²³ who give for cetyl sodium sulphate at a benzene-water interface in the usual units:

$$(F + 0.15)(A - 13.9) = 1.8(kT \times 10^{16}) \quad . \quad . \quad . \quad (36)$$

The agreement of Alexander and Teorell's value of x with the theoretical value of 1.5 shows that values of x greater than unity are likely to be found for ionised films.

The Potential ϕ .

The potential ϕ of the preceding theory is the potential at the position occupied by the "heads" of the adsorbed molecules, and cannot, therefore, be identified with the ζ -potential of the interface, which is the potential at some small distance from the interface. The potentials ϕ and ζ (as determined, say, by cataphoresis of an emulsion stabilised with a detergent) should, however, be closely related. The theory allows ϕ to be found very simply, as follows.

If uni- and di-valent cation salts are added to the aqueous phase, ϕ can be determined from experimental data together with equation (9) and (10); for, using a given concentration of detergent, and adding NaCl and CaCl₂, say, in sufficient amounts to give two solutions of the same interfacial tension, then these equations show that:

$$\frac{n_1}{n_2} = e^{\frac{e\phi}{kT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

²³ Alexander and Teorell, *Trans. Faraday Soc.*, **35**, 727.

where n_1 and n_2 are the concentrations of NaCl and CaCl_2 , respectively. Powney and Addison's data can be used with (37) to determine ϕ . A solution of 5.0×10^{-3} M sodium dodecyl sulphate at 20°C . gives an interfacial pressure of 31.5 dynes/cm. when 3.03×10^{-3} M NaCl or 1.25×10^{-5} M CaCl_2 is added; the value of ϕ from (37) is then 146 millivolts. When 3.0×10^{-5} M NaCl or 6.2×10^{-5} M CaCl_2 are used to give the same interfacial pressure, ϕ is found to be 135 millivolts. This is a reasonable value. Hartley and Roe²⁴ have found that the ζ -potential, which is numerically smaller than ϕ , of cetane sulphonic acid and cetyl pyridinium bromide micelles is of the order of 100 millivolts (the justification for regarding ϕ as approximately equal for a plane surface or a micelle is discussed on page 166).

It is possible that ϕ contributes to the potential of a film measured by usual methods on a Langmuir trough. Consider the potential ϕ_a in the air above the film. Dean, Gatty and Rideal²⁵ have recently given reasons for believing that there is no net charge above the film, i.e. that there is no double layer of ionised air molecules. If this is true right up to the film, then $(\partial^2 \phi_a / \partial x^2)$ is zero. In this case $(\partial \phi_a / \partial x)$ is constant, and must be zero; (if it were constant and finite there would be an infinite potential between the air at infinity and the film). The "potential of the film" as usually measured, ΔV , is thus the sum of the dipole potential and ϕ .

$$\Delta V = 4\pi m\mu + \phi \quad . \quad . \quad . \quad (38)$$

where μ is the vertical component of the dipole moment of a molecule and m is the number per sq. cm. There is as yet no independent method of finding ϕ for a non-ionised or partly ionised film such as a fatty acid; but the present theory allows ϕ to be determined for a completely ionised film. It is proposed to test equation (38) experimentally when conditions permit.

Work of Adsorption.

The work of adsorption of non-ionic surface active species has been estimated from various surface tension measurements.²⁶ The estimate is always made from the formula:

$$c = c_s e^{-\omega/kT} \quad . \quad . \quad . \quad (39)$$

where c is the known bulk concentration, and c_s is estimated from Γ and an arbitrary film "thickness." The present theory gives a new means of estimating μ . The coefficient μ , which is determined from the concentrations of mono- and divalent salts necessary to give one value of surface tension, is $c_s e^{-\omega/kT}$ (cf. equation (14)). Or μ is the concentration of the surface active anion that would give the required surface tension if the ion had zero charge. The concentration μ can, therefore, be compared with the concentration of a similar non-ionic material with the same number of CH_2 groups, say pentadecylic acid, giving the same surface tension.

A direct comparison does not appear to be possible at present between μ for a sodium alkyl sulphate with c for the corresponding acid, because compounds with an odd number of carbon atoms, which one of them must

²⁴ Hartley and Roe, *Trans. Faraday Soc.*, 1940, 36, 101.

²⁵ Dean, Gatty, and Rideal, *ibid.*, 161.

²⁶ Adam, *The Physics and Chemistry of Surfaces* (2nd ed., O.U.P.), 1938.

possess, have been but little investigated. A rough comparison of the two methods can, however, be made, using data for sodium dodecyl sulphate and lauric acid. Powney and Addison give some results on the surface tension of sodium dodecyl sulphate when NaCl or CaCl₂ is added to the solution. Their curves show that a surface tension of 40 dynes/cm. is given by 3.1×10^{-3} N sodium dodecyl sulphate in a solution of 8.7×10^{-3} N NaCl or in 1.8×10^{-3} M CaCl₂. Substitution of these values in equation (20) gives μ as 6.4×10^{-6} N. Frumkin²⁷ gives some values for the surface tension of lauric acid solutions. Unfortunately his data do not quite overlap those of Powney and Addison, but at a concentration of 5×10^{-3} N, the surface tension is around 50 dynes/cm. The two very different means of determining the factor for $c_s e^{-\omega/kT}$ for a 12 carbon atom chain are thus in good agreement. Exact agreement would not, of course, be expected because of the different hydrophilic groups of the two molecules and the difference of one CH₂ group in the chain.

One concludes that values of ω deduced from the present theory of the effect of salts on strong electrolyte surface active materials are in full agreement with those deduced by other means. The actual values of ω can never be accurately determined because of the uncertain value of c_s , but the agreement obtained for $c_s e^{-\omega/kT}$ by the two quite independent methods is evidence for the general validity of the theory.

Critical Concentration for Micelles.*

If the surface of a micelle were plane, the preceding theory could be used to discuss the equilibrium between micelles and free long chain ions in the presence of salts. Some idea of the smallest micelle that may be treated as a plane surface can be obtained by comparing equation (5) with its counterpart for the case of spherical symmetry using the electrical conditions at the surface of the micelle. Assuming only one species of monovalent cations to be the significant ions in bulk, the equation with spherical symmetry is:

$$\frac{d^2\phi}{dr^2} + \frac{2}{r} \frac{d\phi}{dr} = -\frac{4\pi}{D} n_1 \epsilon e^{-\epsilon\phi/kT} \quad . \quad . \quad . \quad (40)$$

where r is the distance from the centre of symmetry. In equation (40), ϕ is largely determined by the effective electric charge at the micelle surface, and the term $n_1 \epsilon$ takes note of the ionic distribution just outside the micelle. Equation (40) differs from that for the case of a plane charged surface by the presence of the term $\frac{2}{r} \frac{d\phi}{dr}$ on the L.H.S.; or, the equation for the plane surface may be written:

$$\frac{d^2\phi}{dr^2} = -\frac{4\pi}{D} n_1 \epsilon e^{-\epsilon\phi/kT} \quad . \quad . \quad . \quad (41)$$

The micelle surface will certainly be appreciably different from a plane surface when:

$$\left| \frac{2}{r} \frac{d\phi}{dr} \right| \approx \left| \frac{d^2\phi}{dr^2} \right| \quad . \quad . \quad . \quad (42)$$

²⁷ Frumkin, *Z. physikal. Chem.*, 1925, **116**, 482.

* Throughout this discussion Hartley's conception of the micelle is assumed.

A rough approximation to $\frac{d\phi}{dr}$ may be obtained by integrating (41) with respect to ϕ , *i.e.* from :

$$\frac{d\phi}{dr} = \left[\frac{8\pi kT}{D} n_1 (e^{-\epsilon\phi/kT} - 1) \right]^{\frac{1}{2}} \quad (43)$$

At the surface of a micelle $\epsilon\phi$ is likely to be around $5kT$; it was found to be $5.3kT$ for the interfaces of Powney and Addison, and the effective surface charge of a micelle will probably be of the same order as the surface charge at these interfaces. Hartley and Roe's measurements²⁴ of the ζ -potential confirm this (see p. 165). If n_1 is taken as $10^{-3} N$, and $\epsilon\phi$ as $5kT$, equation (42) gives r as 40 Å; for a bulk concentration of cations of $10^{-2} N$, r is 13 Å. Hartley and Runnicles²⁸ have shown that the radius of the 16 carbon atom paraffin chain micelles is probably around 26 Å, and for solutions with a total cation concentration of $10^{-2} N$ or more, the surface of these micelles can be roughly regarded as plane, and the present theory should be at least qualitatively applicable.

According to Samis and Hartley,²⁹ the size of the micelles varies slightly with the nature of the gegenions, but if we take it as constant for any one gegenion, then σ is constant (equation (2)) for the micelles of any given "amphipath." The critical concentration for micelles should, therefore, obey equations (16). These relations hold semi-quantitatively for the data of Tartar and Cadle³⁰ on the effect of sodium chloride on the critical concentration of sodium dodecyl and tetradecyl sulphonates. Equation (16.1) is applied to these data (read from the graphs in their paper) in Table III where the last column should be constant. It is evident from the above discussion of the effect of sphericity that (16.1) should be a better approximation the higher the concentration of detergent required to form micelles, *i.e.* the shorter the chain length. This is seen from Table III to be the case.

TABLE III.

[S].	[NaCl].	γ_1 .	$\gamma_1 [S] ([S] + [NaCl]) = 2^2$.	
9.74×10^{-3}	0	0.89	8.5×10^{-5}	dodecyl sodium sulphonate.
8.20×10^{-3}	4×10^{-3}	0.88	8.8×10^{-5}	
7.76×10^{-3}	8×10^{-3}	0.86	10.6×10^{-5}	
2.79×10^{-3}	0	0.94	7.3×10^{-6}	tetradecyl sodium sulphonate.
1.73×10^{-3}	4×10^{-3}	0.92	9.1×10^{-6}	
1.25×10^{-3}	8×10^{-3}	0.90	10.3×10^{-6}	

The theory does not, however, appear to apply even qualitatively for a positive "amphipath" such as cetyl pyridinium chloride. Samis and Hartley²⁹ have shown that the cetyl pyridinium micelle is not formed in lower concentration with sulphate as gegenion than with chloride. Again, they show that the cetyl pyridinium micelle selectively adsorbs chloride ions from a mixture of chloride and sulphate, whereas according to the present theory the sulphate ion should be much more strongly adsorbed. Samis and Hartley suggest that specific forces of adsorption play a part in these phenomena, in which case the theory here developed is inapplicable.

²⁸ Hartley and Runnicles, *Proc. Roy. Soc. A*, 1938, 168, 420.

²⁹ Samis and Hartley, *Trans. Faraday Soc.*, 1938, 34, 1288.

³⁰ Tartar and Cadle, *J. Physic. Chem.*, 1939, 43, 1173.

It is worth noting that the values of λ^2 for dodecyl and tetradecyl sulphonate can be used to estimate the value of $2\Delta\omega$ when two CH_2 groups are added to the chain; for equation (15) gives:

$$\log_e \lambda_1^2 - \log_e \lambda_2^2 = \frac{2\Delta\omega}{kT} \quad . \quad . \quad . \quad (44)$$

where λ_1^2 and λ_2^2 are values for dodecyl and tetradecyl ions, respectively. Inserting values from Table III gives $\Delta\omega$ as $1.2 kT$, which is in reasonable agreement with values deduced from Powney and Addison's data (*cf.* section 1.4).

Summary.

A theory has been developed for the distribution of ions under an ionised monolayer. It explains the fact that only ions of opposite sign to the film have an appreciable effect on the film, and agrees quantitatively with available data on the effect of added electrolytes on the surface and interfacial properties of these films.

It can be used as a guide to the form of the surface equation of state of ionised monolayers. The air-water potential given by a monolayer and the formation of micelles of long chain ions in the presence of salts are discussed in the light of the theory. The theory provides a new method of calculating the work of adsorption of long chain molecules.

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SOME FACTORS GOVERNING THE STABILITY OF OIL-IN-WATER EMULSIONS.

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Although intensive research has been devoted to emulsions because of their practical applications, there has been, until recently, a lack of quantitative data which has rendered difficult any detailed discussion of their stability.

All emulsions are thermodynamically unstable systems since the globule size progressively increases. Also, after certain periods of time, which may differ very widely for different emulsion systems, the internal phase liquid separates rapidly or slowly to form a distinct layer. This process is essentially irreversible.

Since the separation of internal phase is extremely slow in many systems—emulsions may not "break" for several years—search has been made for some other characteristic feature of an emulsion which may be taken to represent stability, some property which may be measured accurately and rapidly. Several methods based on this

general approach are available, but are entirely empirical in nature and often quite unsuitable for comparison of stabilities of dissimilar systems. It must be said at the outset, therefore, that there is no single property of an emulsion other than rate of coalescence or separation of internal phase that can be considered to constitute stability.

It is sometimes stated that the degree of dispersion of an emulsion indicates its stability and that a simple size-frequency examination will therefore suffice for its measurement. It appears, however, from results to be discussed later, that stability is not necessarily related to degree of dispersion and therefore all comparisons based on this conception are fundamentally unsound. Further confusion exists in the literature by the phenomenon of creaming being regarded as instability. Creaming is the sedimentation of the dispersed globules by gravity without coalescence and is manifest by the separation of a layer of *external* phase liquid.

Verwey¹ terms emulsion stability, as defined above, "secondary" stability, while his "primary" stability refers to the ease of emulsification of a system.

While a preliminary study of emulsion stability will be concerned only with the degradation of a system with time, it is important also to recognise and measure the effect of environmental changes, especially temperature and those brought about by the addition of electrolytes. Some of these have already received considerable study which has yielded information fundamental to emulsion theory, but much of this work (and especially that concerning the effect of electrolytes) has been done with oil hydrosols. Generalisations from the study of such systems may be completely misleading. It is necessary, therefore, to outline the properties of the different classes of emulsion.

Emulsion Classes.

Three fundamentally different classes of emulsion can be recognised :

- (1) oil hydrosols (unstabilised emulsions) ;
- (2) emulsions stabilised by electrolytes ;
- (3) emulsions stabilised by emulsifying agents in the ordinary sense, which may be (a) colloidal materials or (b) finely divided solids.

Oil Hydrosols.

These are obtained from two liquid phases without the addition of an emulsifying agent and are characterised by three prominent features: (a) they only contain a fraction of 1 % of internal phase liquid, (b) their preparation usually involves considerable application of energy, (c) they are generally of the oil-in-water type only.* These characteristics differentiate oil hydrosol from stabilised emulsions and it is conventional to regard the former as unstabilised systems. The decidedly more hydrophobic nature of oil hydrosols supports this conclusion. Verwey² disagrees, however, with this differentiation and claims that there is no essential difference between the stabilised emulsion and the oil hydrosol since all liquids will contain sufficient concentration of impurities to promote the formation of these very dilute systems. What

¹ Verwey, *Chem. Rev.*, 1935, **16**, 363.

* See, however, Cheesman and King, who report the existence of "water oleosols."

² Verwey, *Chem. Weekblad*, 1939, **36**, 800.

these impurities are and how they function is not postulated. From the work of Cheesman and King³ it appears that very small concentrations of stabilising substances favour the formation of water-in-oil emulsions rather than of the opposite type. The idea that oil hydrosols are stabilised only by impurities should therefore be treated with reserve.

Emulsions Stabilised by Electrolytes.

A preliminary description of these systems has been published by Cheesman and King.³ A number of electrolytes in small concentration are capable of stabilising emulsions of polar liquids and water, both types being obtainable according to the method of shaking, but the water-in-oil type being much the more stable. The different effects of various salts is due especially to the position of the anion in the lyotropic series and stability is almost certainly to be discussed in terms of the diffuse double layer. While emulsions stabilised by the presence of inorganic salts are not commonly met with, colloidal electrolytes such as the soaps are capable of functioning in this manner if present in great dilution. Thus, sodium oleate, when present in an emulsion in a concentration of ca. 1 % as normally, will promote an emulsion of the oil-in-water type, while the opposite type is readily formed if the concentration of the soap is relatively much less. This explains many anomalous results which are obtained in emulsion practice.

Stabilised Emulsions.

By far the commonest type of emulsion is that which is stabilised by the presence of an emulsifying agent in sufficient concentration to form at least a unimolecular layer. These agents are generally colloids, either of the highly hydrated, gel-forming type (gums, gelatine) or else colloidal electrolytes (soaps, sulphonated oils); solid particles are also capable of stabilising emulsions if they also can be adsorbed at the interface. It is generally agreed that the stability of these emulsions is due to the presence of an adsorbed film at the interface, consisting of (a) a coherent, mechanically strong gel, (b) an orientated unimolecular layer, or (c) tightly packed solid particles. Nevertheless many other factors contribute or are alleged to contribute to emulsion stability. Some of the more important of these will now be discussed in connection with the oil and water type of system which has received most study.

Stability of Emulsions.

Measurement of Stability.

As already mentioned, the only significant method of measuring stability is one which considers the coalescence of the dispersed droplets of an ageing emulsion or the separation of free internal phase liquid from it. In those systems where oil separation is relatively fast and well defined, mere measurement of its extent after different times will suffice for comparison of stability. The results plotted in Fig. 1, obtained by Dr. Wrzeszinski in this laboratory illustrate this clearly. More precise data may be obtained by making a size-frequency analysis of an emulsion when freshly prepared and at various times thereafter and plotting specific area of interface against time. In the system repre-

³ Cheesman and King, *Trans. Faraday Soc.*, 1940, 36, 241.

sented by Fig. 1 results obtained by the size frequency method corresponded closely with those shown by the curves. King and Mukherjee⁴ have applied the size-frequency method with some success and were able to compare emulsions prepared with different agents and under different conditions. Unpublished work by Gilpin shows, however,

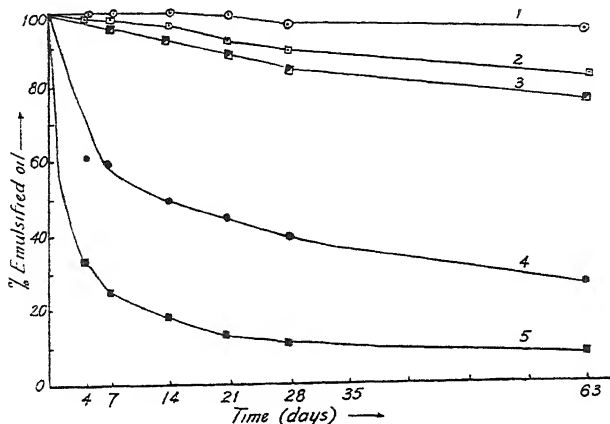


FIG. 1.—Separation of oil from sodium stearate stabilised emulsions and potassium sulphate.

Curve.	○ 1.	□ 2.	■ 3.	● 4.	■ 5.
Concn. NaOl (%) . . .	0.25	0.075	0.075	0.25	0.075
Normality of K ₂ SO ₄ . . .	0	0	0.006	0.06	0.06

that the method may give misleading results in certain cases, especially where the concentration of emulsifying agent is small.

Emulsifying Agent and Stability.

Qualitative results indicate well enough the differences in stability of emulsions stabilised by agents of widely different character, but for less obvious cases the size-frequency method is alone capable of giving significant results. King and Mukherjee were able to study, for example, the different stabilities of emulsions of the same oil stabilised by different soaps.

Some results plotted in Fig. 2 illustrate the essential difference in characteristics of emulsions stabilised by colloidal electrolytes, hydrophilic colloids and by solids. The soap-stabilised emulsion is initially very highly dispersed as compared with the other two, but deteriorates relatively quickly, so that, after 30 days it is actually less highly dispersed than the other emulsions. In fact, much of the oil originally dispersed had separated as a free layer by this time.

The gelatin-stabilised emulsion, while originally less highly dispersed than the first is much more stable and shows only a gradual decrease in

⁴ King and Mukherjee, *J. Soc. Chem. Ind.*, 1939, 58, 243; 1940, 59, 185.

the area of interface. In this system, in distinction to the last, there was no separation of free oil, even after weeks.

A still higher stability characterises the emulsion stabilised by gelatinous alumina in spite of its initial coarseness. Indeed, some emulsions of this type in the author's possession have shown no oil

separation during a period of two years and only slight decrease in the specific interface.

It thus appears that emulsion stability is not, in general, a function of the degree of dispersion. The emulsions illustrated in Fig. 2 might be taken to indicate that the coarser systems are the more stable, but this is not necessarily general. If strictly analogous systems alone are discussed, it seems probable that an optimum degree of dispersion exists for maximum stability. Thus with emulsions stabilised by sodium, potassium and ammonium soaps, those emulsions with the highest degree of dispersion

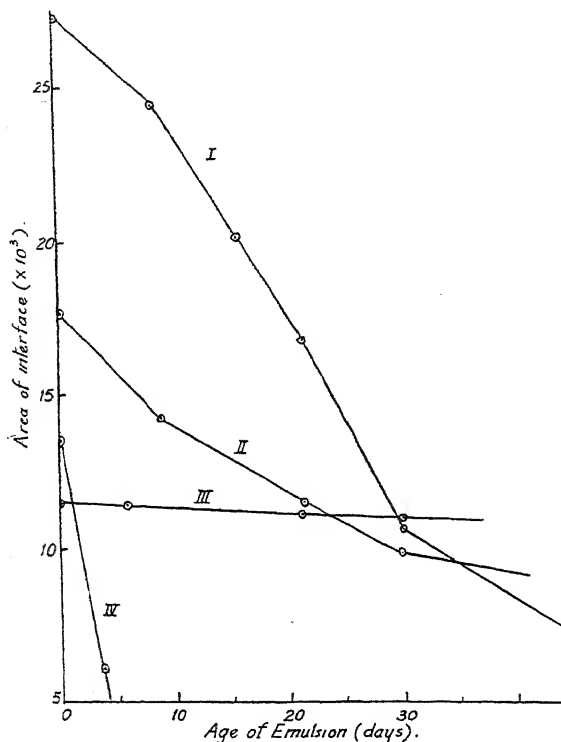


FIG. 2.

- I Sodium stearate stabilised emulsion.
- II Gelatine stabilised emulsion.
- III Inert alumina stabilised emulsion.
- IV Sodium stearate stabilised emulsion + 3 % calcium chloride.

(the majority of the droplets were of diameter $0.5-1\mu$) are the most stable. With emulsions stabilised by inorganic hydroxides, coarser dispersions are more stable than finer ones.

Interfacial Tension.

Although substances which lower the interfacial tension between oil and water are amongst the best known emulsifying agents, the interfacial tension plays a doubtful role in the stability of emulsions. Even apart from the solid agents, many of the newer emulsifying agents which form clear, colloidal dispersions are without appreciable influence on the surface tension of water and yet promote very stable emulsions. It would thus appear that with soaps and other emulsifying agents which do produce lowering of interfacial tension, it is not this property *per se*

which is the important stability factor, but the interfacial adsorption which accompanies it.

Low surface tension is, however, the chief condition favouring ease of emulsification. Those systems recently described by Schulman and Cockbain,⁵ for example, emulsify spontaneously, whereas with solids a large area of interface must first be created by violent agitation and this mechanically produced emulsion stabilised by fine particles of the solid.

The Influence of Electrolytes.

A considerable amount of study has been devoted to the action of electrolytes on emulsions, especially with regard to the phenomenon of phase inversion and to electrical theories of emulsion stabilisation. Bhatnagar,⁶ for example, ascribed the formation of oil-in-water and of water-in-oil emulsions to preferential adsorption at the interface of negative or of positive ions respectively. King and Wrzeszinski,⁷ however, have shown that many systems cannot be converted from the oil-in-water to the water-in-oil type of emulsion by the addition of polyvalent cations even in high concentration. Indeed, the generalisation may be made that if the emulsifying agent is incapable of reacting with the added salt and is present in sufficiently high concentration, the effect of the salt is not fundamental.

Nevertheless, even in these cases where chemical reaction does not take place, electrolyte addition usually leads to coarsening and instability of the emulsion. This is illustrated in Fig. 1 which shows the effect of potassium sulphate on the stability of emulsions promoted by sodium oleate. The untreated emulsion is relatively both fine and stable, but with increasing concentration of potassium sulphate it becomes progressively coarser and less stable. Size-frequency measurements on this system give similar results and show that there is an initial decrease in specific area of interface on the addition of potassium sulphate and that the decrease is more marked the lower the concentration of sodium oleate used. It may be that this electrolyte effect is due to salting out of the soap adsorbed at the interface. Further mention of this will be made under "hydration" below.

Electrical Charge on Emulsion Droplets.

Apart from a few experiments by Limburg⁸ most of the work on the electrical properties of emulsions has been restricted to oil hydrosols in which stability decreases as charge is removed. Some workers, including Verwey² believe that electrical conditions play a dominant role in the stability of all kinds of emulsions; the function of the emulsifying agent is said to be "to shift the potential drop of the electrical double layer towards the outer phase." A study of the effect of electrolytes on the cataphoresis of emulsions stabilised by agents of different type has recently been carried out in this laboratory;⁹ some typical results are shown in Fig. 3 for a saponin-stabilised system. It will be noticed that the emulsion (oil in water) is originally negatively charged and that charge reversal is brought about by aluminium and

⁵ Schulman and Cockbain, *Trans. Faraday Soc.*, 1940, **36**, 651.

⁶ Bhatnagar, *J. Chem. Soc.*, 1920, **117**, 542; 1921, **119**, 61, 1760.

⁷ King and Wrzeszinski, *Trans. Faraday Soc.*, 1939, **35**, 741.

⁸ Limburg, *Rec. trav. Chim.*, 1926, **45**, 772, 854.

⁹ King and Wrzeszinski, *J. Chem. Soc.*, 1940, 1513.

thorium sulphates but not by any of the other electrolytes. In those cases where the electrophoretic velocity was reduced to small values by the addition of electrolytes in concentrations of less than 0.001 N (as with magnesium sulphate and potassium iodide) measurements were also made with much higher concentrations. In no instance was a reversal of sign of charge effected; at very high electrolyte concentrations cataphoretic flow comes to a standstill, however, owing to disturbances due to electrolysis; this, of course, is a general and not a specific property of electrolytes.

Similar results were obtained with systems stabilised by other emulsifying agents, and have been fully discussed in the paper mentioned above.

The chief interest of these results is in the lack of relationship between electrical charge and stability. This was verified by preparing saponin-stabilised emulsions (negatively charged) and adding aluminium sul-

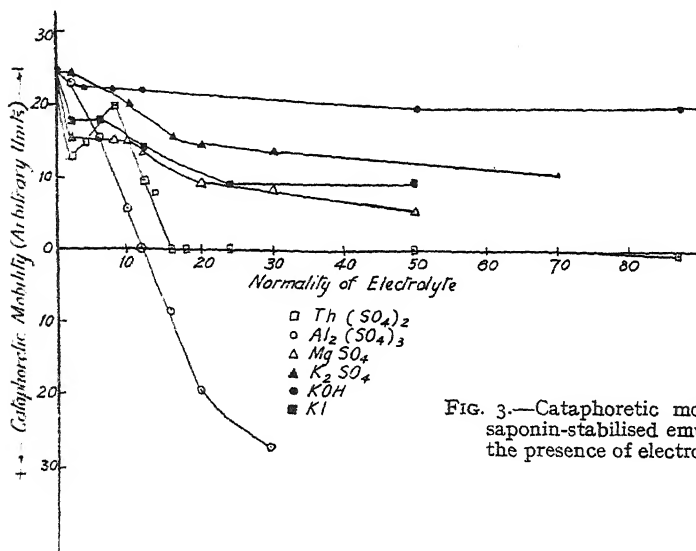


FIG. 3.—Cataphoretic mobility of saponin-stabilised emulsions in the presence of electrolytes.

phate in the proportions to produce an isoelectric and a positively charged emulsion; all these were stable for a period of several months. While they all showed a tendency to creaming and clumping, this was much more marked in the positively charged system than in the others. The isoelectric emulsion was certainly hardly less stable than that which contained no added electrolyte. Under similar conditions a sodium oleate-stabilised emulsion broke rapidly, presumably owing to the formation of aluminium oleate which favours the promotion of emulsions of the water-in-oil type. We have therefore to conclude that, when no chemical reaction takes place between electrolyte and emulsifying agent, the electrical charge on the dispersed droplets does not determine stability or type.

Lyotropic Effects.

In the experiments on the effect of electrolyte addition on cataphoretic velocity of emulsion droplets, no anionic effect could be observed;

presumably therefore, the lyotropic influence of the various salts was either unimportant, or else inoperative owing to the dilution necessary for the experimental measurement of cataphoresis by the ultramicroscope method. A study was therefore made of the effect of different anions on concentrated emulsions. The results with saponin-stabilised emulsions were typical for the colloid stabilised type of system. The addition of sulphates preserved or even increased the stability while at the same time leading to a marked increase in the viscosity of the emulsion. Iodides and thiocyanates, on the other hand, yielded very mobile emulsions which quickly broke. The nature of the cation seemed to be unimportant in these experiments.

Rather unexpectedly the effect of the salts on systems stabilised by solids, of which bentonite and inert alumina were chosen as representative, was found to be exactly the opposite; sulphates quickly broke these emulsions while thiocyanates and iodides increased viscosity and stability.

The reason for this fundamental difference between emulsions stabilised by colloids and those by solids is probably to be found in the degree of dispersion of the two types of stabiliser. The colloids are very finely dispersed while the solids are, relatively, very coarse. Iodides and thiocyanates are remarkable for their peptizing properties, while the sulphate ion at the other end of the lyotropic series has a coagulating influence. Presumably there is an optimum particle size for the protecting particles at the emulsion interface, as has been suggested by Bechhold and collaborators¹⁰ to explain the emulsifying properties of various clays. Particles of solid emulsifiers may approach this optimum dispersion when peptized by thiocyanates and iodides, while saponin particles under the same conditions approach too nearly molecular dispersion to be efficient stabilisers. The flocculating effect of the sulphate ion is, as might be expected, of minor importance in the case of the highly dispersed colloids, while with the solids the coarsening it produces is very detrimental to emulsion stability. The peptizing effect of thiocyanates and iodides on alumina suspensions is marked by a great increase of the sedimentation volume, while with saponin it causes the turbidity of the solution to disappear. The sulphate has the opposite effect on both these dispersions.

Viscosity.

While there is no evidence that viscosity by itself can explain emulsion stability, it is certainly true that viscous emulsions are generally more stable than mobile ones. The stabilising effect of high viscosity must be recognised as functioning by the retardation of the coalescence of the individual droplets and is generally noticeable in highly hydrated systems which are, in any case, resistant to disruptive influences. High viscosity must often be regarded, then, as a symptom rather than as a cause of stability in emulsion systems.

The viscosity of an emulsion is a function, not only of the proportion of internal phase liquid, but of the nature and condition of the emulsifying agent. Work (unpublished) carried out in this laboratory by Hess has shown that, for a given oil concentration, the viscosity of oil-in-water emulsions can vary widely with the emulsifying agent, even when the latter do not form viscous suspensions in water. Thus an emulsion

¹⁰ Bechhold, Dede and Reiner, *Koll. Z.*, 1921, 28, 6.

stabilised with "Daxad 45" and containing 75 % of oil was relatively mobile, whereas with most other emulsifying agents, products of a paste-like consistency are obtained with this amount of oil. It is not surprising therefore that the emulsions described in the previous section, stabilised by agents of varying degree of dispersion, should also show remarkable viscosity differences.

The viscosity of the internal phase liquid is of little importance in determining the viscosity of the emulsion which it forms. Thus saponin-stabilised emulsions of petroleum jelly and of a mobile paraffin gave almost identical viscosity curves up to 60 % internal phase.

Nature of the Internal Phase.

It is well known that some liquids are much more difficult to emulsify than others and that the ease of emulsification does not merely depend on viscosity, nor on chemical relationships between the two liquid phases and the emulsifying agent. In a preliminary investigation of this factor by Wrzeszinski emulsions of a number of liquids and mixtures of liquids were prepared by means of sodium oleate. The oils differed both in density and polarity. The main characteristics of the emulsions are compared in Table I. A space between two adjacent lines denotes a marked difference in the ease of emulsification or in stability between two successive emulsions, while brackets indicate that these differences are small.

TABLE I.

No.	Agent.	Density.
Order of Ease of Emulsification (Emulsifying Ability).		
1	Mixture of kerosene and carbon tetrachloride	1.00
2	Mixture of kerosene and nitrobenzene	1.00
3	Mixture of benzene and nitrobenzene	1.00
4	{ Kerosene	0.80
5	{ Kerosene containing 0.1 % oleic acid	0.80
6	{ Benzene	0.88
7	{ Carbon tetrachloride	1.58
8	Mixture of carbon tetrachloride and nitrobenzene	1.40
9	Nitrobenzene	1.20
Order of Stability on Ageing and Resistance to K_2SO_4.		
1	Mixture of kerosene and carbon tetrachloride	1.00
2	Mixture of kerosene and nitrobenzene	1.00
3	{ Kerosene	0.80
4	{ Kerosene containing 0.1 % oleic acid	0.80
5	{ Benzene	0.88
6	{ Mixture of benzene and nitrobenzene	1.00
7	{ Carbon tetrachloride	1.58
8	Nitrobenzene	1.20
9	Mixture of nitrobenzene and carbon tetrachloride	1.40

It is noticeable that, in general, the smaller the difference in specific gravity between the two liquids, the greater is the ease of emulsification and the stability, nitrobenzene and a heavy mixture containing nitrobenzene being exceptions. It might perhaps be inferred that there is something inherent in the nature of nitrobenzene, possibly its strong polarity which is an adverse factor in emulsion formation and stability. No data are available as to the relationship between chemical properties

and emulsion stability, but it is safe to say that this factor as well as density is operative.

Emulsifying Agent Concentration.

According to the theories based on the idea of a condensed uni-molecular film, there should be a critical concentration of emulsifying agent above which the emulsion is stable and below which it will break in a short time. Also the adverse effects of electrolyte addition should become more marked below this concentration. Rough calculation shows that for agents such as sodium oleate this value should be of the order of 0.5 % calculated on the weight of oil phase. The value deduced from the results of Fischer and Harkins¹¹ is of the same order. Some experiments were carried out by Dr. Wrzeszinski to determine whether such a critical concentration does, indeed, exist.

For this purpose emulsions were prepared with varying concentrations of emulsifying agent and treated with varying amounts of salts known to be chemically inert towards the agent. The agents chosen were sodium oleate and saponin which were treated with potassium sulphate and aluminium sulphate respectively.

In the soap-stabilised emulsions which were untreated with the salt, no critical limit of agent concentration is apparent, but with the electrolyte treated systems a border line of stability clearly exists between the soap concentrations 0.10 % and 0.05 % respectively. With saponin-stabilised emulsions there appears to be a material difference in stability both for treated and untreated systems between agent concentrations 0.02 % and 0.01 %.

These results by themselves offer only limited support to the idea of a critical concentration, since the stability changes are in no way abrupt. It appears certain, however, that the more extended the layer of agent at the interface, the more sensitive it is to the influence of electrolytes. This is a feature which must be appreciated for the valid comparison of the results of different workers.

Concentration of Internal Phase Liquid.

Although it is possible to prepare emulsions containing a very high concentration of internal phase, such systems are relatively less stable than those containing a small proportion of the same liquid. They have a tendency to suffer phase inversion which may or may not take place, depending on the mechanical properties of the interfacial film. Solid stabilisers do not normally form flexible layers and are thus unable to resist the steric influences favouring phase inversion; this is shown clearly by bentonite emulsions.

The effect of electrolytes is likewise greater in concentrated than in dilute emulsions, at least in as far as the lyotropic effect is operative.

Temperature.

It is well known that the breaking of emulsions is rapidly accelerated by increasing the temperature. It has been suggested that examination at a temperature higher than room temperature might form a quick and useful method of comparing emulsion stabilities. Results obtained by the size-frequency method show, however, that the effect of heating

¹¹ Fischer and Harkins, *J. Physic. Chem.*, 1932, **36**, 98.

is much greater for some types of system than for others; for example, soap-stabilised emulsions break rapidly on heating to 80° C. whereas those stabilised by inert solids are only slightly less stable at this temperature than normally. There is therefore no real basis of comparison here.

The effect of freezing and thawing is likewise specific for the emulsifying agent employed.

Mechanical Methods of Emulsification.

In a paper by Cheesman and King¹² it has been shown that the method of shaking two immiscible liquids together with the emulsifying agent may condition the type of the resulting emulsion. Similarly it is often found in industry that a slight modification of the emulsification technique may lead to the production of the unexpected type of emulsion.

Different mechanical treatments may lead to differences of stability as well as of dispersion. This is clearly shown in the size-frequency study of soap-stabilised emulsions by King and Mukherjee.⁴ For emulsions stabilised by a number of soaps, the specific area of interface was approximately ten times greater in homogenised than in hand-shaken, systems, while the stabilities were approximately in the ratio 1.8:1. With an emulsion stabilised by 1% sodium oleate solution, however, the shaken emulsion, although possessing only 1/18th of the specific interface of the corresponding homogenised specimen was actually more stable.

A fundamental difference between systems produced by those two types of mechanical treatment is shown by the dispersion analyses quoted in Table II. With the freshly prepared homogenised emulsion,

TABLE II.—PERCENTAGE DISTRIBUTION OF OIL DROPLETS OF DIFFERENT SIZE IN HOMOGENISED AND HAND-SHAKEN EMULSIONS STABILISED BY POTASSIUM OLEATE.

Age of Emulsion (days):— Mean Diameter (μ).	Homogenised.					Hand-Shaken.				
	0	7	14	21	30	0	7	14	21	30
0.5	62.5	51.1	30.5	25.6	21.0	36.1	31.4	25.0	21.8	16.5
1.0	—	—	—	—	—	—	—	—	—	—
1.5	25.3	30.4	38.8	38.4	37.6	23.9	18.9	22.0	15.7	17.6
2.5	8.2	11.8	18.2	20.7	22.0	14.6	15.0	15.0	14.2	19.0
3.5	3.2	4.4	7.7	9.6	11.3	9.4	10.4	10.8	11.6	10.6
4.5	1.1	2.0	4.0	4.5	3.6	6.0	8.6	8.0	9.7	8.7
7.5	—	0.3	0.8	1.2	2.0	3.6	4.4	5.0	5.9	7.3
12.5	—	—	—	—	0.5	3.0	6.0	5.5	7.3	6.7
20	—	—	—	—	—	2.4	3.1	4.0	6.2	5.9
30	—	—	—	—	—	1.5	2.2	3.0	5.4	4.5
42.5	—	—	—	—	—	—	—	1.5	2.2	3.2
62.5	—	—	—	—	—	—	—	—	—	2.1
Free oil (%)	—	—	—	6.25	22.5	—	—	—	—	—

the greatest number of dispersed droplets are in the 0.5 μ range with only a few as large as 4.5 μ . As the emulsion ages, the number of larger particles increases somewhat, but there are practically none of diameter

¹² Cheesman and King, *Trans. Faraday Soc.*, 1938, 34, 594.

larger than 7.5μ . Nevertheless in the older emulsions there is considerable accumulation of free oil. Thus many emulsions, even when half broken, still contain the remainder of their oil dispersed in droplets as small as when freshly prepared. From these results, which are typical, it is tempting to conclude that homogenised, soap-stabilised emulsions are only stable when the particles are of diameter $0.5\text{--}7.5 \mu$, and that, in the course of time, the proportion of larger particles increases at the expense of the smaller ones until 7.5μ is reached. Thereafter further growth produces larger particles which are unstable and coalesce rapidly, creaming and separating as free oil. With hand-shaken emulsions prepared with the same agent quite another state of affairs exists. Here the dispersion is initially much coarser and there are many droplets of diameter greater than 7.5μ , the maximum of the homogenised systems, while there are some droplets as large as 42.5μ in the freshly prepared sample. Under the conditions of emulsification by hand-shaking these larger droplets seem to be hardly less stable than the smaller ones and grow to form increasingly larger drops, which finally separate. In some of the older emulsions, drops of diameter as large as 100μ are not uncommon. There appears, therefore, to be some fundamental difference in the mechanism of breaking of similar emulsion systems, prepared by different mechanical means. This is probably to be attributed to differences in the interfacial film structure, but what these differences are cannot yet be suggested.

Solid-Stabilised Emulsions.

A recent survey¹³ of the emulsifying properties of inorganic solids shows that a gelatinous structure and a basic nature facilitate stabilisation. The hydrous oxides and hydroxides are amongst the most effective of solid agents and aged aluminium hydroxide which can be prepared in a form very inert towards acids and alkalis, is the best approximation to the ideal solid emulsifying agent. Emulsions prepared with the aid of this substance are rather coarse but extremely stable towards electrolyte addition and temperature change. For example, an emulsion of carbon disulphide in water, stabilised by inert alumina, is indefinitely stable and no decomposition can be observed, while in a similar emulsion stabilised by soaps, the carbon disulphide decomposes completely within a few weeks. The alumina stabilised emulsion can be boiled without breaking or conflagration. Such emulsions, stabilised by inert solids, can be saturated with calcium or aluminium salts without suffering phase inversion or oil separation, although the droplet size increases somewhat.

Additions of minute concentrations of surface tension depressors together with solid stabilisers results in the production of much finer dispersions than can be obtained with the solids alone, but this extra degree of dispersion is easily lost by slight environmental changes which are incapable of influencing the film of solid.

The antagonistic effects of solid and of colloidal emulsifying agents in combination have had but little study. R. K. Thomas, working in this laboratory, has shown that sodium oleate which by itself promotes emulsions of the oil-in-water type, actually increases the power of carbon black to produce the water-in-oil type. This is presumably due to orientated adsorption of soap molecules on the surface of the carbon,

¹³ Bennister, King and Thomas, *J. Soc. Chem. Ind.*, 1940, **59**, 226.

increasing the hydrophobic nature of the latter. In a similar manner sodium oleate decreases the emulsifying ability of aluminium hydroxide.

General Conclusions.

The results quoted in this paper, together with those of other recent workers on emulsions, point to the strength and compactness of the interfacial film as the most important single factor favouring stability; indeed there is little to distinguish between the stability of the film and of the emulsion respectively. Most of the other influences are effective essentially in as far as they modify the properties of the film. Nevertheless these other factors, subsidiary though they may be, are of very definite importance both with regard to the stability and physical properties of the emulsified system; it is therefore important that their significance should be recognised.

Amongst these factors, emulsifying agent concentration has perhaps been too little stressed by previous investigators. It appears, for instance that, with a sufficiently high concentration of the agent, the electrical behaviour of the emulsion will bear an insignificant relation to its stability, as is exemplified by the high order of resistance of such emulsions to the action of added electrolytes. It may be concluded, indeed, that the stability of an emulsion of moderately high oil concentration is only seriously affected by the addition of electrolytes, if the amount of agent is insufficient to form a coherent film round the oil globule. The lower the concentration of the emulsifying agent, the weaker is its protective action and the more do the properties of the emulsion resemble those of a lyophobic colloid.

In conclusion, therefore, it may be said that the typical stabilised emulsion of the oil-in-water type possesses hydrophilic properties, especially when there is present excess of the emulsifying agent, and may be regarded as a combination of and intermediate between a hydrophilic and a hydrophobic colloid. This picture of the stabilised emulsion is very similar to that of a protected colloid.

The author desires to express his thanks to Drs. Cheesman, Mukherjee and Wrzeszinski and to Messrs. Gilpin, Hess and Thomas who have worked so enthusiastically in his laboratory, attempting to obtain a comprehensive view of emulsion structure and behaviour.

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THE STABILISATION OF WATER-IN-OIL EMULSIONS BY OIL-SOLUBLE SOAPS.

BY R. C. PINK.

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Up to the present only a small number of polyvalent metal soaps have been shown to possess the power of stabilising water-in-oil emulsions. Newman¹ examined among other materials the oleates of magnesium, calcium, zinc and nickel and found that of these soaps only

¹ *J. Physic. Chem.*, 1914, 18, 34.

magnesium oleate and to a less extent calcium oleate gave stable dispersions. Briggs and Schmidt² confirmed Newman's results and pointed out for the first time the striking differences between such oil-continuous emulsions and the water-continuous emulsions stabilised by alkali metal soaps. The former are characterised by the absence of regularly shaped globules and by very rapid "creaming."

It has been suggested recently that the stabilisation of water-in-oil emulsions by magnesium oleate is dependent on the fact that practically all of the soap is precipitated from the oil phase in the presence of a small amount of water.³ The soaps studied by Newman together with a number of metallic stearates have now been prepared and the effect of water on their benzene solutions examined.

Experimental.

The oleic and stearic acids were obtained from Kahlbaum and the other chemicals used were of "AnalaR" standard. The soaps were prepared by metathesis of the corresponding sodium salt in aqueous solution. This method is unsatisfactory if carried out in the cold because of the possibility of occlusion of the colloiddally-dispersed sodium soap. The reaction was therefore carried out at 90° and the precipitated soap was repeatedly washed by grinding in a mortar with distilled water. Nickel oleate, which, owing to its stickiness at ordinary temperatures, cannot satisfactorily be washed in this manner, was recrystallised from pyridine.

The Effect of Water on Benzene Solutions of the Soaps.

2 % solutions of the soaps in benzene (distilled over sodium) were prepared and 50 c.c. portions of these solutions were shaken with an equal volume of water on a mechanical shaker for 24 hours. The resulting emulsions were broken (if necessary, by centrifuging) and the concentration of soap remaining in the benzene layer estimated.

A number of the soaps prepared (*i.e.*, zinc, calcium, strontium, stearates and barium oleate) were insufficiently soluble in dry benzene to be included in this series of experiments. Barium oleate is peculiar in that while the dry soap is insoluble in benzene it disperses readily at the boiling point when a trace of water or aqueous alcohol is added. On cooling, the solution sets to a clear gel and on standing, white flocculent material is precipitated. The results obtained with the remaining soaps are shown in Table I. It will be observed that a negligible precipitation of soap occurs with the oleates of nickel and zinc.

It has already been shown³ that with magnesium oleate precipitation is practically complete in the presence of very small amounts of water (0.22 % by volume in the case of a 2 % solution) and, further, that the precipitated material is hydrated soap. The precipitation may occur in the following way. In dry benzene the anhydrous soap exists in the form of micelles, in which, it may be assumed, the hydrocarbon parts of the molecules are oriented to the outside. When such a micelle comes into

TABLE I.

Soap.	% Soap in Benzene Layer after Shaking with Water.	
Oleates—		
Magnesium	0.05
Calcium	0.32
Strontium	0.85
Nickel	1.98
Zinc	1.97
Stearates—		
Magnesium	0.04
Nickel	0.12

² J. Physic. Chem., 1915, 19, 478.

³ Pink, J. Chem. Soc., (a) 1938, 1252; (b) 1939, 619.

contact with water at the oil-water interface water molecules may penetrate into the interior of the micelle and become attached to the polar groups of the soap molecules. The effective diameter of the polar group will thus be increased to such an extent as to render the structure of the oil soluble micelle unstable and a more stable structure with the polar group on the outside of the micelle will be formed. Such a micelle would be insoluble in oil. An analogous overturning of the molecules must be postulated to explain the observation of Devaux ^{4, 5} that stearic acid which is normally hydrophobic becomes hydrophilic in contact with water. In order to explain the fact that the precipitated soap is also insoluble in water it must be assumed that the polar group $(-\text{COO})_2\text{M}$, though sufficiently hydrophilic to render the micelle insoluble in oil is yet insufficiently hydrophilic to confer upon it the power of dissolving in water. This concept of a relation between "balance" and solubility of long chain molecules is not a new one and has in fact been dealt with recently in some detail by Dean.⁶ It will be seen that the question whether magnesium oleate will be hydrophilic or hydrophobic is not dependent on any intrinsic property of the soap molecule but depends rather on the structure and arrangement of the micelle. The amount of water necessary to bring about the change in the structure of the micelle will, of course, depend on the degree of stability of the hydrophobic arrangement. It is difficult to understand why the oleates of zinc and nickel are not precipitated in the same manner as the other soaps examined. A similar difficulty has been encountered in connection with multilayers. It has already been noted that stearic acid in contact with water becomes hydrophilic. On the other hand, a built-up multilayer of barium stearate does not become hydrophilic in contact with water and, more remarkable, it is also oleophobic to hydrocarbons, in spite of the fact that the hydrocarbon part of the molecule is supposed to be oriented to the outside.⁵

The Stability of Water-in-Oil Emulsions.

The emulsions were prepared by shaking equal volumes (50 c.c.) of a 2 % soap solution and water, first by hand by the method recommended by Cheesman and King ⁷ for the production of water-in-oil emulsions and then on a mechanical shaker for 24 hours. Observations of the stability of the resulting emulsions were carried out immediately after removal

TABLE II.

Soap.	Time required for First Sign of Separation.	Time for Complete Separation.	Remarks.
Magnesium oleate .	None after 7 days	—	Good emulsion.
Calcium oleate .	40 secs.	4 mins.	Very poor emulsion.
Strontium oleate .	30 secs.	2 mins. 15 secs.	Very poor emulsion.
Nickel oleate .	12 secs.	75 secs.	No emulsification.
Zinc oleate .	12 secs.	70 secs.	No emulsification.
Magnesium stearate .	None after 7 days	—	Good emulsion.
Nickel stearate .	None after 7 days	—	Good emulsion.

from the shaker. No satisfactory method, other than size-frequency analysis, has yet been devised for the detection of small differences in the stability of emulsions. On the other hand, where great accuracy is not required, the stability of emulsions prepared under the same circum-

⁴ Devaux, *Ann. Report Smithsonian Inst.*, 1913, 261.

⁵ Cf. Schulman, *Ann. Reports Chem. Soc.*, 1939, 109.

⁶ *Wetting and Detergency*, 1937, London, p. 25.

⁷ *Trans. Faraday Soc.*, 1938, 34, 594.

stances can be compared by measuring either (1) the time required for the first visible sign of separation of the two phases or (2) the time required for complete separation. When the latter is not too great it is convenient and more accurate to make both measurements. The relative stabilities of the emulsions prepared in the manner described are shown in Table II.

Discussion.

From a comparison of the results shown in Tables II and III it can be seen that where no precipitation of soap occurs in contact with water there is no evidence of emulsifying power. On the other hand, all the soaps precipitated are not satisfactory emulsifying agents (*e.g.*, the oleates of calcium and strontium). It is clear that the nature of the precipitate is important. If the precipitated soap is to act as an emulsifier it must fulfil a number of conditions:—

(1) It must be practically insoluble in both phases. It is known that a benzene solution of ethanolamine oleate gives a bulky precipitate of hydrated soap when shaken with a small amount of water and that viscous oil-continuous emulsions are formed when excess water is added.⁸ If sufficient water is added or if the water-in-oil emulsions are allowed to stand the hydrated soap dissolves in the aqueous phase and an inversion of type occurs.

(2) The precipitated soap must remain at the interface. This will be the case only if the solid is partially wetted by both liquids. If wetted more easily by water than by oil it lies further into the water phase and the emulsion is water-continuous; if wetted more easily by oil the solid lies further into the oil phase and water in oil emulsions result.

(3) There must be sufficient lateral adhesion between the solid particles.

It should be noted that the stabilising film is essentially a solid and has therefore a certain rigidity. It is this rigidity of the stabilising film which gives to the emulsion globules their characteristic irregular shape. Schulman and Cockbain⁹ have deduced recently that a film of this type is necessary for the stabilisation of oil-continuous emulsions, pointing out that in the case of oil in water emulsions, water, being an ionising medium, enables charged droplets to repel one another; whereas when oil is the continuous phase a film consisting of charged molecules could not prevent the water globules from coalescing because oil, being a non-ionising medium, no electrical diffuse layer or ionic atmosphere could be built up. This fundamental difference in the two types of emulsion is reflected in the more rapid creaming which is so characteristic of the oil-continuous type. Since practically all of the soap is precipitated from solution in the presence of exceedingly small amounts of water it is evident that, provided the concentration of soap originally dissolved in the oil phase is fixed, the amount of precipitated soap available for the formation of the stabilising film is independent of the phase ratio. Consequently in emulsions in which the ratio water to oil is small there may be a considerable surplus of hydrated soap above the amount necessary for the formation of the film. In such emulsions microscopic examination reveals the presence of masses of soap floating in the oil phase.

⁸ Pink, *J. Chem. Soc.*, 1939, 53.

⁹ *Trans. Faraday Soc.*, 1940, **36**, 661.

There is another factor of importance in the stabilisation of water-in-oil emulsions. The reduced interfacial tension brought about by the soap^{3b} permits easy subdivision of the water in the oil and thus, by bringing the phases into intimate contact, assists in the precipitation of the stabilising film.

It will be seen from Table II that even with magnesium oleate and magnesium and nickel stearates a small amount of soap remains in the oil phase. If the presence of precipitated soap is essential for emulsion

stability it is to be expected that a concentration of soap greater than this value will be necessary to give stable emulsions. That this is true in the case of magnesium oleate is shown in Table III.

The emulsions were prepared by shaking 50 c.c. of the benzene solution with an equal volume of water on a mechanical shaker for 24 hours.

TABLE III.

% Concentration of Magnesium Oleate in Benzene.	Time required for Visible Sign of Separation of Phases.
0.02	15 secs.
0.05	25 secs.
0.07	37 secs.
0.10	4 hours.
0.20	30 hours.
0.30	3 days.

Since many polyvalent metal soaps are insoluble in oil they cannot be used to prepare water-in-oil emulsions by the direct method described. With such soaps water-in-oil emulsions can be obtained indirectly by inversion of the corresponding water-continuous system. Emulsions can, of course, be prepared indirectly with soaps which are soluble in oil, but it should be noted that in either case the precipitated soap must satisfy the conditions stipulated above if it is to give stable emulsions. Thus it was found that when oil-in-water emulsions prepared by shaking equal volumes of 2 % sodium oleate and benzene were inverted by addition of the necessary electrolytes only magnesium oleate gave satisfactory dispersions. No emulsification was produced with nickel or zinc oleates and only very unstable emulsions were obtained with the calcium barium and strontium soaps.

Summary.

(1) The effect of water on benzene solutions of a number of polyvalent metal soaps has been examined.

(2) Oil soluble soaps which are precipitated from solution when shaken with water give rise to stable water-in-oil emulsions provided the precipitated soap fulfils the following conditions:—

- (a) It must be insoluble in both phases.
- (b) It must remain at the interface, *i.e.*, it must be partially wetted by both liquids.
- (c) There must be sufficient lateral adhesion between the solid particles.

(3) Stable water in benzene emulsions are obtained with magnesium oleate, magnesium stearate and nickel stearate but not with the oleates of calcium, barium, strontium, zinc or nickel.

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THE OIL/WATER INTERFACE.

A GENERAL DISCUSSION.

Thursday, 9th January, 1941.

A GENERAL DISCUSSION of the Faraday Society was held jointly with the Physical Society at the Hotel Rembrandt, London, S.W. 7, on Thursday, 9th January, 1941, from 11 A.M. to 4 P.M., to discuss "The Oil/Water Interface."

The President of the Faraday Society, Professor E. K. Rideal, occupied the Chair throughout the meeting. Some 60 members of the two societies were present. Instead of the usual informal Guest Night Dinner, a very pleasant luncheon was taken in the Hotel during an interval in the meeting. At the conclusion of the meeting thanks were accorded with acclamation to Professor Emeléus and his colleagues of the Imperial College of Science for providing the epidiascope and other conveniences at the hotel, as well as to the authors of the papers which had stimulated so useful a discussion.

The papers appear in the preceding pages from page 117 onwards and the report of the discussion thereon is in the following pages.

GENERAL DISCUSSION.

On Dr. Alexander's Paper.

Mr. R. C. Palmer (*Leeds*) said: How far can the value given in this paper for C for cetyl sodium sulphate be regarded as an approximation to the theoretical value of $3/2kT$.

Prof. N. K. Adam (*Southampton*) said: The values of C in Table II are much higher than the theoretical value of kT , i.e., 400 at room temperature in the units employed here, for a perfect gaseous film. Can any explanation be given of this?

It seems curious that surface potential measurements can be made on the oil-water interface, using a polonium electrode, if the electrode is in the air and above a thin layer of oil, but not if the electrode is in the oil. In the earlier paper of Alexander and Teorell, the authors said that the alpha rays from the polonium were absorbed in the oil if the polonium electrode was in the oil; but it is not easy to see why they are not equally absorbed when they start in the air and then have to pass through the oil.

Dr. R. K. Schofield (*Harpenden*) said: Regarding the equation of state, a plot of FA against F is generally more revealing than that of F against A . A quantity of special interest is the limiting value of the product FA for very small values of F . The equation $(F - F_0)(A - A_0) = C$ fails to give this because it is obviously inapplicable to values of F below F_0 . I suspect that the $FA-F$ curve is not straight, but its slope increases as F decreases and that as $F \rightarrow 0$, $FA \rightarrow kT$. If so, the values found for A_0 and C by drawing the best straight line will depend on the F range of the experimental observations.

The Chairman said: The apparent value of C must necessarily depend upon F since it is derived from the Boyle-Charles law, inapplicable to films except in the highly extended gaseous state.

Dr. A. E. Alexander (*Cambridge*), in reply, said: The value of C is only equal to kT for substances with unionised head-groups, whereas all the compounds shown in Table II are ionised ones. Langmuir has derived an equation for the effect of the electrostatic repulsive forces between the orientated dipoles constituting the monolayer.¹ This gives values of the right order only if the dielectric constant of the aqueous medium is taken as round about 20. Cassie and Palmer have shown that their theory and assumptions lead to a value of C equal to $3/2kT$, i.e., ca. 600, which is in reasonable agreement with experiment.

With regard to the second point this is an experimental observation. It may be due to leakage when the polonium electrode is in the benzene layer, owing to the lower resistance of the benzene as compared with that of the air.

The C values are thought to be accurate to about 15 %. Thus, on the whole, the values are in reasonable agreement with that of $3/2kT$ (ca. 600) predicted by the theory of Cassie and Palmer.

On the Papers by Dr. Danielli and Dr. Frazer.

Dr. R. A. Kekwick (*London*) said: Observations by Dr. A. S. McFarlane on human serum in the Tiselius electrophoresis apparatus indicate that the fat globules migrate with the β globulin boundary. This suggests that the globules are covered with a layer of β globulin, which would also explain their tendency to aggregate at about pH 5.3.

Dr. J. F. Danielli (*Cambridge*) said: Results closely analogous to those of Frazer and Stewart on extracellular proteins have also been obtained with intracellular proteins. Harvey and Shapiro² showed that the tension at the surface of oil droplets inside living cells (marine eggs) was very low, about 0.6 dynes/cm. Danielli and Harvey³ showed that this was due to the adsorption of an intracellular globulin on the surface of the oil. In the presence of intracellular albumins and globulins the globulin was preferentially adsorbed. Other fats or lipoids in fine division, responsible for the cloudy or opalescent appearance of protein preparations made by grinding the eggs with sand and centrifuging off fat globules and heavy detritus, were also associated with the globulins and only to a much smaller extent with the intracellular albumins. This was shown by fractional precipitation with ammonium sulphate.

Subsequent observations⁴ on haemoglobin, pepsin, trypsin, ovalbumin and sturin showed that the ability to reduce the tension at the surface of oils to a very low value is a common feature of many proteins.

The observations on the adsorption of hormones and toxins of protein character on oil droplets raises the question of whether they are adsorbed in a primary denatured layer or in a secondary layer of native globular protein. If insulin were adsorbed in the denatured condition its physiological activity would probably be greatly reduced. If adsorbed in the native state the process is probably reversible and in this case the adsorption process would have a buffering action, tending to maintain the blood insulin level at a constant value.

Dr. A. E. Alexander and Dr. J. F. Danielli (*Cambridge*) said (*partly communicated*): Frazer has pointed out that the isoelectric point of the protein protected emulsions he studied was about 5.3, corresponding very closely with that of native β -globulin. Ham, while introducing the papers of Dickinson and Growney, pointed out that the isoelectric point of proteins adsorbed on quartz, as determined by electrophoresis, also agreed closely with that of the native protein determined by other methods (e.g.,

¹ Langmuir, *J.A.C.S.*, 1932, **54**, 2798.

² Harvey and Shapiro, *J. Cell. Comp.-Physiol.*, 1933, **5**, 255.

³ Danielli and Harvey, *ibid.*, 1934, **3**, 483.

⁴ Danielli, *Cold Spring Harbor Symposia*, 1938, **6**, 190.

precipitation).¹ The explanation is probably as follows. At an interface between an aqueous protein solution and a second phase which may be gaseous or liquid, there exists a primary protein monolayer upon which a secondary layer of globular native protein is adsorbed. When the second phase is solid possibly only the globular layer is adsorbed, although in view of the high I.T. normally thought to exist at the solid/liquid interface formation of the primary layer might also be expected. The primary protein layer which may be identified with the usual monolayers studied at the A/W and O/W interfaces, would bring about the main reduction in I.T., and in view of its insolubility may be termed "surface denatured." The secondary adsorbed layer would primarily determine the electrophoretic properties, and hence the isoelectric point of the globular form would be obtained. Secondary adsorption of native protein would also explain the residual enzymic activity of adsorbed layers of urease and pepsin,² and the abnormal thicknesses of certain protein multilayers,³ and adsorbed monolayers.⁴

It would be of great interest to study the electrophoresis of particles covered with the primary or "surface denatured" film only, since the isoelectric point thus obtained might well differ from that for the native protein, and a difference between the solid/liquid and liquid/liquid interfaces might also be observed.

Prof. N. K. Adam (*Southampton*) said: Was the fat emulsion which neutralised the insulin stabilised by protein or not? If not, presumably the mechanism of neutralisation was a simple adsorption on the fat-water surface of the emulsion.

Both Frazer and Schulman (using monolayers) find that globulins are as a rule more easily adsorbed on fatty substances than albumens. Frazer's fat-water surfaces are presumably liquid, and I doubt if they could manifest any very high degree of specificity. I wonder if the preferential adsorption of globulins, over albumens, is possibly due to the globulins containing a higher proportion of hydrophobic material in their composition than the albumens?

Dr. J. H. Schulman (*Cambridge*) said: Preliminary observations on the effect of injecting various components of serum into a physiological solution beneath a monolayer composed of esters, show striking differences. In one case a liquid film of an ester such as kephalin or triolein will gelatinise and the surface pressure rise from a film pressure of 2 dynes to 25 dynes due to a minute concentration of one serum component. Another serum component, although forming a gel film on the free aqueous solution, will not affect the liquid ester film. These differences appear to be due to the different proteins in the serum components, which were separated by the Tiselius method, and form an analogy to the results obtained by Frazer. The differences in adsorption of the various serum components on to esters either in the form of monolayers or emulsions was attributed by me to the lipoids associated with the serum components, rather than any structural differences in the hydrophobic hydrophilic balance in the pure globulin or albumin.

The lipoids of the lecithin or kephalin type could associate with specific polar groups in either the globulin or albumin fraction and thus radically change the adsorbing properties of these protein fractions.

Dr. K. G. A. Pankhurst (*London*) said: I should like to ask Frazer whether the variation of the degree of distribution and of mobility of fat particles in plasma with pH was a reversible phenomenon. Was it possible, for example, to redisperse the clumps of particles precipitated

¹ Abramson, *Electrokinetic Phenomena*, 1934.

² Langmuir and Schaefer, *J.A.C.S.*, 1938, **60**, 1351.

³ Dean, Gatty and Stenhagen, *Nature*, 1939, **143**, 721.

⁴ Langmuir, *Cold Spring Harbor Symposia on Quantitative Biology*, 1938, **6**, 171.

at the isoelectric region and at pH less than 2 by subsequent appropriate adjustments of pH , or was the precipitation in strong acid an irreversible degradation reaction?

The Chairman said: The isoelectric point of proteins adsorbed on quartz appears to be identical with that of the protein determined in bulk phase by cataphoresis. Since the change in mobility of the particle can be determined in presence of increasing concentrations of protein, *i.e.* the adsorption isotherm, it would appear that in this substrate the primary adsorbed layer only is being considered.

Dr. D. Jordan Lloyd (London) said: Adam asks if there is any difference in the composition of serum albumin and serum globulin to account for their differences in behaviour. Some of the available figures are not very recent but one can say with certainty that the albumin contains more lysine residues which would contribute a higher number of charged centres which would also be centres of hydration. As regards the other acid and basic groups there does not appear to be much difference but the analyses are not recent. Albumin contains no glycine residues which are present in globulin. As regards the long hydrocarbon chain contributed by leucine there is about the same amount in both proteins.

Dr. A. C. Frazer (London) said: In reply to Schulman, with emulsions albumin appears to afford protection but the particles protected in this way have quite different properties from those treated with a mixture of albumin and globulin. There seems to be no doubt that globulin is preferentially associated with the fat particles and that the behaviour of the particles is dependent upon this film. In the blood stream the particles also appear to be associated with the globulin fraction of the plasma protein.

In reply to Danielli, I agree that the film was most resistant affording protection against acids and salts. The question as to whether detoxication of toxin was a similar mechanism appears to be answered by the fact that toxin can be recovered from the oil/water interface. This would imply that no denaturation had occurred. It may be that the primary globulin film forms the foundation upon which the further protein structure incorporating the toxin is built. Thus the toxin would be part of the globular film and could be released by decrease of interfacial area. The toxin experiments were made using a broth filtrate in which globulins would be present. In the absence of globulin it is possible that detoxication might occur by involvement of the toxin in a primary film under which circumstances one would not expect to recover potent toxin.

In reply to Keckwick, I suggest that although the B globulin is most closely associated with the fat particles, it is not impossible that other globulin fractions were involved in the outer ring, which would still modify their action on the body cells. If one considered that the plasma architecture could only be modified to include foreign protein material by beginning with a new foundation of orientated globulin, then that foundation might be at the oil/water interface.

In reply to Adam, I agree that the fact that globulin is more hydrophobic than albumin may explain globulin adsorption. On the other hand, a type of specificity is apparent in toxin adsorption since the addition of diphtheria toxin to emulsion followed by tetanus toxin did not protect against the latter, whereas if the toxins are reversed, the animals injected died of diphtheria toxæmia. In all cases enough emulsion was present to detoxicate many times the total amount of toxin added. If one starts with the orientated globulin foundation and on this build up a new protein architecture including and detoxicating one toxin, a second toxin would not fit into this pattern.

In reply to the Chairman (Prof. Rideal): With the emulsions both the albumin and globulin fractions protected separately. With albumin-globulin mixtures, globulin must be at least predominating at the inter-

face. The lack of association between fat and albumin as described by Keckwick suggests that the albumin is not internally placed. Schulman also found no film formation with albumin.

In reply to Danielli, I suggest that the presence of phospholipid in the membrane might account for the association of the albumin with the red blood cell.

On Dr. Hartley's Paper.

Dr. A. B. D. Cassie (*Leeds*) said: Do these branched chain salts show ageing of surface tension? As Alexander (*this discussion*) has observed, ageing of surface tension is not due to electrostatic phenomena, and surface active ions that show no surface tension ageing might be expected to exist. This information would be very useful for experimental verification of the theory of soluble ionised monolayers put forward by Cassie and Palmer.

Dr. A. E. Alexander (*Cambridge*) said: In view of a recently suggested explanation for the phenomenon of "surface ageing,"¹ it would be extremely interesting to see how these branched chain salts compare with their straight-chain analogues. An increased time lag would, in general, be expected. Surface tension measurements with sulphonates have recently been shown by Langmuir and Waugh² to be very sensitive to even the minute amounts of divalent cations which are present in good grades of distilled water (10^{-7} M).

Dr. A. J. Ham (*Liverpool*) said: Matthews³ has made certain measurements of the I.T. between cyclohexane and solutions of various carbohydrates. The lowering of I.T. obtained is much less than in Hartley's experiments with paraffin-chain salts, but it is interesting to note that the type of I.T. lowering *v.* concentration curve obtained by Matthews could be related to the shape of the molecules constituting the interfacial film. Linear molecules lowered the tension rapidly at first but soon a limiting value was reached, whereas more spherical molecules gave a steady and continuous lowering as the concentration of carbohydrate was increased.

Dr. G. S. Hartley (*Winterslow*), in reply to Dr. Alexander, said: My results do not indicate that the branched-chain salts are slower in reaching the final I.T. than the straight chain, except that the compound R(14,2) was exceptionally slow. A more thorough investigation of very dilute solutions would be needed to establish any such effect.

I am familiar with the very great effect of traces of divalent metals, as this phenomenon was encountered by Dr. Conmar Robinson when at University College. He found that anomalous minima in dilute solutions, present when water from a tin-lined copper still was used, disappeared when water distilled in quartz and stored in pyrex was used. In the light of this experience, my own work was done with water of this latter quality only. No divalent metal came in contact with the salts during preparation.

Only in the case of compound R(14,2) for cyclohexane and of all the salts for benzene was there a steady downward drift of drop-size with increasing time of formation. It must be noted that compound R(14,2), like other unsymmetrical ones in this series, is a mixture of two isomers. The difference between these will be more marked than in the less unsymmetrical compounds. It is possible that one isomer is more rapidly adsorbed and afterwards replaced by the other. Benzene is a good solvent for these potassium salts, and the drift in this case is presumably due to slow diffusion of the adsorbed salt into the bulk of the growing drop.

¹ Alexander, *Trans. Faraday Soc.*, 1941, 37.

² Langmuir and Waugh, *J.A.C.S.*, 1940, 62, 2771; cf. Stenhagen, *Trans. Faraday Soc.*, 1940, 36, 496.

³ Matthews, *Trans. Faraday Soc.*, 1939, 35, 1113.

On Dr. Schulman's Paper.

Dr. A. J. Ham (*Liverpool*) said: It should be noted that curves of Type I, showing only small increasing changes of mobility with rising pH are all those obtained for solid hydrocarbons and esters. In view of the known change in electrophoretic mobility with change of state, it would be wiser to designate this the "solid type" of curve. Schulman's interpretation of curve Types II and III is a very welcome contribution, correlating his own work with our electrophoretic results. Williams had concluded that Type II curves were given by molecules of low molecular weight able to undergo a change in configuration with pH ; this change now appears as one from one of no mutual orientation to a *cis* configuration.

Liquid hydrocarbons do not give either of the types of curve mentioned, and likewise large-chain acetates pass from curves of Type I to this "liquid hydrocarbon" type on melting. The rotation of the acetyl CH_3 group about $C-O$ or CH_2-O bond may render adsorption of OH^- by the acetate group comparable to that for a CH_3 group.

In his biological section Schulman finds that *trans* or unoriented molecules are indigestible, whereas *cis* molecules are readily digested. It is of interest that long-chain compounds containing a double bond and capable of *trans* or *cis* forms, exist in nature in the *cis* forms only. Thus oleic acid and oleyl alcohol are found, but not the corresponding elaidyl compounds; the higher melting-point of the *trans* compounds may be an important factor however.

Prof. N. K. Adam said: I feel some difficulty in accepting the view that *solid* compounds have one type of curve relating electrophoretic mobility to pH , while *liquid* compounds have a quite different one. If this difference in type of the mobility- pH curves were due wholly to the comparatively accidental circumstance of the substance being above, or below, its melting-point, one would expect a sudden change in the type of curve of such a substance as pure octadecane, as the temperature is raised from below to above the melting-point. Is the change in fact *sudden* at this point? I know that there are changes in the structure of solids, which occur some distance between the melting-point, but even these are usually well-defined transitions occurring at one temperature only, and I doubt if a gradual change of type of the mobility curve could be accounted for if solidity was the only, or even the principal, factor in deciding the type of mobility curve.

I have felt for some time past that a tendency has grown up to use the formerly quite definite terms, *solid* and *liquid*, in a very loose way, so much so that in some phenomena I have actually heard of monolayers which are, physically, quite fairly mobile in the surface, referred to as "solid." I think it would be better to retain the old meaning of these terms, namely that liquidity occurs when the translatory motions of the molecules are freed. So far as I know, this occurs at a definite temperature.

The observations on lipolysis made by Schulman show some correlation with the partition hypothesis of fat absorption.¹ According to this theory, hydrolysed fat passes to the liver, but unhydrolysed fat travels by the lymphatic route to the systemic blood and fat depots. It has recently been observed that short chain fatty acids tend to accumulate in the liver during fat absorption. The difference in the hydrolysis of the long and short chain fatty acids may be another factor concerned in partition.

Dr. A. E. Alexander (*Cambridge*) said: The X-ray measurements of Müller show quite definitely that no abrupt change in the lattice spacing occurs at the melting-point, so no abrupt change in electrophoretic properties would be expected (see the contribution to the papers of Dickinson and Growney).

Dr. R. K. Schofield (*Harpenden*) said: There is, so far as I am aware, no evidence, apart from electrophoresis, to support the idea that negative interfacial charges can arise by direct adsorption of OH^- ions. Normally such charges arise from the dissociation of H^+ ions from $\text{HO}-$ groups. The measurements of Powney and Wood seem to show that very low surface concentrations can affect the electrophoretic mobility. It is, therefore, possible that OH^- ion adsorption occurs to so small an extent that it can only be detected by electrophoresis.

Dr. A. J. Ham (*Liverpool*) said: Melting occurring sharply over 0.1°C . or so cannot be denied, when the test of "sharpness" is the visible change from a rigid solid to a liquid. Changes in the solid lattice before the melting-point is reached may occur abruptly, but there is evidence of a relatively slow lattice expansion.¹ The translatory motion of molecules in the surface layer may increase before the melting-point is reached, while the bulk of the solid remains much more rigid. Thus in quite a different investigation Garner and co-workers² find it necessary to assume "mobility of surface atoms of the absorbent," in this case oxides such as Cr_2O_3 —well below their melting-points.

Williams³ suggested not a gradual change before melting, but after it, *i.e.*, the persistence of orientation and some type of structure in the liquid state. Evidence for such a cybotactic state is very considerable⁴ and the existence of some "solid" properties just above the melting-point seems to be established.

This appears to be sufficient to warrant our assumption that the difference in mobility- pH curves observed over the region of the melting-point is due to a gradual transition of the surface from its state in a solid well below the melting-point to that in a solid well above the melting-point. The transition true solid true liquid does not appear to occur abruptly at one temperature, when referred to the surface of long-chain hydrocarbons and esters under our experimental conditions. Alexander⁵ has a useful suggestion as to the reason why liquid surfaces should possess a higher negative charge than solid surfaces of the same substance.

Dr. J. H. Schulman (*Cambridge*), in reply, said: It would be very interesting to compare the electrophoresis of suspensions of ethyl butyrate and ethyl valerate or ethyl benzoate and benzoyl propionate with pH . The marked difference in the digestion of these esters by pancreatin suggests that the indigestible esters of the above-mentioned compounds would follow type II and the easily digestible esters type III. This would show that the small molecules such as ethyl butyrate fall in the same category as the large ones such as ethyl myristate which can exist in the *cis* form. The intermediate compounds can orientate themselves in either the *cis* or *trans* form according to their environment.

I am in agreement with Kitchener's and Ham's explanation for the gradual adsorption of OH^- ions found experimentally over the melting-point of hydrocarbons, instead of an expected jump at the melting-point as suggested by Adam.

On the Papers by Dr. Dickinson and Dr. Gowney.

Dr. A. E. Alexander (*Cambridge*) said: With regard to the very marked increase in electrophoretic mobility which occurs with hydrocarbons on transition from the solid to the liquid state, as observed by Williams

¹ Müller, *Proc. Roy. Soc., A*, 1930, **127**, 417.

² Garner and Ward, *J. Chem. Soc.*, 1939, 862; Garner and Dowden, *ibid.*, 893.

³ Williams, *Trans. Faraday Soc.*, 1940, **36**, 1042.

⁴ Discussion of Liquid Crystals, *ibid.*, 1933, **29**, 881.

⁵ Alexander, *this discussion*.

and mentioned by Dickinson, rotation of the long chains, resulting in more complete screening of the negative terminal carbon atom by the positive hydrogen atom, would appear to be insufficient. More probable is an increase in the penetration by water molecules as the temperature increases beyond the melting-point. The electrophoretic measurements of Williams¹ with octadecane resemble the lattice structure as shown by X-rays in showing no abrupt change at the melting-point.² From the experiments discussed below water penetration might be anticipated to occur in the region around the melting-point and not sharply just at that point. Thus careful examination might show time effects in this region, the mobility increasing with the time.

The above picture is really an elaboration of the well-known increase in solubility on liquefaction, and leads to an increase of charge and hence of mobility regardless of whether this is ascribed to OH⁻ or other anion adsorption. Thus it is complementary, rather than contradictory, to Danielli's suggested explanation.³

With solid crystals, as shown by the work of Stenhagen⁴ on the attack of built-up films of methyl stearate by N. NaOH, and by the work of Newitt⁵ on the hydrolysis of tristearin by acid and alkali, there is an extremely slow penetration into the lattice. With fluid interfacial films, however, the rate of penetration is very rapid. The difference is particularly well shown by Sebba's work⁶ on the evaporation of water through condensed monolayers on water. Sebba observed a slow expansion and increased water permeability of monolayers of *n*-docosanol or arachidic acid on standing, particularly at large areas, which he ascribed to the formation of double molecules lying flat on the surface, but which would appear to fit in better with a slow hydration of the long chains.⁷

The hydration of polar groups when these are present may also be a factor to be considered, and might explain the unusual mobility order observed by Dickinson with the halides. As he points out, the low values observed, as compared with those for a liquid hydrocarbon, indicate orientation with the halide groups towards the aqueous phase. If the mobility were determined solely by the charge on the end halogen atom then the order $R \cdot Cl < R \cdot Br < R \cdot I$ would be expected, whereas any hydration effect would be in the opposite order. A combination of these two effects might account for the observed order of $R \cdot I > R \cdot Cl > R \cdot Br$.

Dr. J. A. Kitchener (*London*) (*communicated*): There has been some discussion on the distinct electrophoretic behaviour of solid fat particles as compared with liquid fats. No doubt the lower mobility of the solids is due to a reduction of the number of ionic groups in the interface through orientation of the molecules in a crystal lattice. Comment has been made on the fact that rise of temperature is said to produce a gradual transition from the mobility characteristic of the solid to that for the liquid, without any sudden discontinuity such as would be expected at a change of phase. Even if melting occurs by way of several smectic states, the change of mobility with temperature might be expected to take place in corresponding steps, and not gradually.

The explanation of this apparent anomaly is probably simple. The electrophoretic mobility depends only on the outer layer of molecules, and these, at sufficiently low temperatures, will be fixed in the crystal lattice. As the temperature is raised, increasing the rotation and vibration, the surface molecules will "melt" before the true melting-point is reached because they are bound into the crystal on one side only. Such

¹ Williams, *Trans. Faraday Soc.*, 1940, **36**, 1042.

² Müller, *Proc. Roy. Soc., A*, 1930, **127**, 417.

³ Danielli, *this discussion*.

⁴ Stenhagen, *Trans. Faraday Soc.*, 1938, **34**, 1328.

⁵ Newitt and others, *J.C.S.*, 1937, 876.

⁶ Sebba, *ibid.*, 1940, 106, 114, 128.

⁷ Alexander, *Trans. Faraday Soc.*, 1941, **37**.

surface sintering is to be expected in all solids; an example is the ease with which the "active centres" of many contact catalysts are destroyed by rise of temperature. Since corners sinter first, followed by edges, and then plane faces, the change of the surface will be gradual and will not be determined by the melting-point of the interior of the crystal. When surface molecules have escaped from their position in the lattice they will, no doubt, orient with their hydrophilic group in the aqueous phase, thus increasing the surface density of charge. According to this idea, solid fats should attain an electrophoretic mobility virtually equal to that of the liquid drops at temperatures distinctly below their true melting-point.

Dr. A. J. Ham (*Liverpool*), in reply, said: Alexander's suggestions as to the possible reasons for the anomalous behaviour of alkyl bromides in Dickinson's research, and for Growney's results, are very welcome; no theory was advanced by the authors.

The increase in mobility observed on passing the melting-point of the dispersed substance has been incompletely investigated; further work should serve to test the explanation offered for the observed intermediate states of surfaces between "true solid" and "true liquid" types.

The lowering of mobility in the case of alkyl chlorides compared with hydrocarbons (Dickinson's paper) would be much better shown if in Table II the value of 3.18 had been inserted for hydrocarbon mobility. This is the value for a *liquid* hydrocarbon with which the liquid halides used should be compared.

Dr. J. F. Danielli (*Cambridge*): The assumption that the negative charge of ester and hydrocarbon particles, in, e.g., $N/100$ NaCl, is due to specific adsorption of OH^- ions, is open to many criticisms. At pH 7 the bulk ratio $[\text{Cl}^-]:[\text{OH}^-]$ is about 10^5 , and at pH 4 is about 10^8 . Hence, to get adsorption of even *equal* numbers of OH^- and Cl^- ions, the difference in decreases in potential energy on adsorption of the two ions would be 6,800 cal. at pH 7, and 10,900 cal. at pH 4. These are rather large differences, though perhaps part of the difference in adsorption could be due to steric factors, and the potential energy difference correspondingly reduced. But it seems advisable to consider first how far non-specific mechanisms may account for the observed charge. The three non-specific mechanisms which may give rise to unequal distributions of ions in the region of the interface are (1) ionisation of inorganic groups; (2) distribution of ions around the ends of dipoles orientated at the interface; and (3) partition phenomena. With a pure hydrocarbon it is possible that (3) only is important. In this case the partition coefficient of the different ions between hydrocarbon and water will be different, and probably follow roughly the same order as the hydration of the ions, the more hydrated ions having the lower hydrocarbon-water partition coefficients. Thus with NaCl solutions, Na^+ probably has a lower partition coefficient than Cl^- ; in this case, since electrical neutrality is preserved in the interior of the two bulk phases, the partition coefficient of Cl^- will be lowered, and that of Na^+ raised, by the building up of a potential difference across the interface, such that the hydrocarbon side of the interface has a negative charge, and the aqueous side a positive charge. If this suggestion is correct, the negative charge of hydrocarbons at, say, pH 7, is mainly due to Cl^- having a higher oil-water partition coefficient than Na^+ . The changes in mobility at pH more acid and more alkaline than 7 may reasonably be due to the increasing concentration of OH_3^+ and OH^- ions. The change in mobility on melting will mainly be due to changes in partition coefficients (see Alexander's contribution to the discussion).

The negative charge of air-bubbles may also be regarded as due to partition of ions between the surface and bulk phases. Surface tension studies show that the more hydrated an ion, the lower is its surface/bulk partition coefficient (or the more it is desorbed from the surface). As

anions are usually less hydrated than cations, air bubbles in solutions of the common salts will usually be negatively charged.

In the case of the esters, the distribution of ions around interfacial polar groups must also be considered. Surface potential measurements show that the electrical dipoles of surface films of esters are orientated with their negative ends directed towards the aqueous phase. Hence, as Rideal, Gatty and Dean¹ have pointed out, there will be a cloud of positive ions round the negative ends of the dipoles, *i.e.* in the aqueous phase, and a cloud of negative ions around the positive ends of the dipoles, *i.e.* in the non-aqueous phase. These anions in the surface of the non-aqueous phase will increase the negative charge of the ester particles. The magnitude of this effect will, of course, depend on the degree to which stable orientation of the esters occurs. So it is possible that the negative charge of esters in the region of pH 7 is due to the combined action of factors (2) and (3) in causing an excess of Cl^- ions to enter the non-aqueous side of the ester-water interface. Variation of charge with pH may again be reasonably ascribed to the OH_3^+ and OH^- ions in the acid and alkaline regions respectively.

Dr. A. J. Ham (*Liverpool*), in reply, said: The OH^- ion appears to play an important and unique part in the determination of the negative charge on ester and hydrocarbon particles. Variations in OH^- concentration affect the mobility over concentration ranges where other anions have a negligible effect.² There is evidence that a layer of pure water exists at the interface—see Dickinson's paper in this discussion, where the possibility, that this layer partially dissociates, thus forming an OH^- layer, is discussed. It is admitted that OH^- ion is preferentially adsorbed, although the bulk concentration of Cl^- is much greater than that of OH^- .

Reference is made to the "non-specific" nature of the mechanism suggested by Danielli, compared with specific adsorption of OH^- ions. If, however, other mono-valent cations replace Na^+ (*e.g.*, K^+ , Cs^+ , Li^+),³ or if different buffer solutions are used,^{3, 4} the observed values of mobility at each pH are only very slightly affected. A much greater difference would be expected if in each case the partition coefficients between hydrocarbon and water of the individual ions were concerned. In all cases examined OH^- ion is present and pH is all-important.

Primary OH^- adsorption affords the most simple explanation for which no alternative generally applicable to all cases has as yet been given. Schulman's⁵ paper serves to emphasise the utility of the assumption of OH^- adsorption as the primary source of the negative charge, affording as it does good correlation between results at oil/water and air/water interfaces.

The effect of oriented dipoles at the interface has been considered as an important factor in determining OH^- adsorption;⁶ while the third factor mentioned, *i.e.* ionisation of inorganic groups, is recognised as a separate factor operating in some cases together with OH^- adsorption.⁷

Dr. A. E. Alexander (*Cambridge*) said: It would seem that a ready interpretation of the curves in Gowney's Fig. 1 is obtained by assuming that the adsorbed film of stearic acid at the surface of the ethyl laurate droplets is a liquid one. A considerable amount of evidence would indicate this, from observations on stearic acid at the A/W interface, and from the behaviour of various compounds at the O/W.⁸ The tendency of stearic

¹ Rideal, Gatty and Dean, *Trans. Faraday Soc.*, 1940, **36**, 161.

² Roberts, *ibid.*, 1937, **33**, 647.

³ *ibid.*, 1936, **32**, 1705.

⁴ Kohler, *Z. physik. Chem., A*, 1931, **157**, 113.

⁵ Schulman, *this Discussion*.

⁶ Dickinson, *this Discussion*; Williams, *Trans. Faraday Soc.*, 1940, **36**, 1042.

⁷ Lewis and Price, *ibid.*, 1933, **29**, 1181.

⁸ Alexander and Teorell, *ibid.*, 1939, **35**, 727; Askew and Danielli, *ibid.*, 1940, **36**, 785.

acid to be preferentially adsorbed at the ethyl laurate/water interface would be very high on account of its greater hydrophilic end group and its low solubility in this oil phase.

If this assumption of a liquid interfacial stearic acid film is correct then the much greater mobilities of the solutions as compared with the acid alone are readily ascribable to the difference in phase, since at 25° C. stearic acid is a solid and, as is well known, substances show a much lower mobility in the solid as compared with the liquid state.¹

Dr. A. E. Alexander and Dr. J. F. Danielli (*Cambridge*): It seems unlikely on several grounds that the high mobilities shown by esters in the region *pH* 7-13 can be due exclusively to specific adsorption of OH⁻ ions, for the concentration of hydroxyl ions at the surface of the ester particles would be extremely high, *e.g.*, many of the esters (*e.g.*, ethyl laurate) have a mobility of 5 μ /volt/cm./sec. at *pH* 8, which is little changed at *pH* 13: this corresponds to a charge density of about 1.3×10^{13} electronic charges² per cm.² The hydroxyl ions assumed to give rise to this charge are assumed to be held to the surface by specific forces. This being so, the thickness of the layer in which the presumed adsorption occurs must be very small, restricted to the immediate vicinity of the interfacial polar groups, *i.e.* to a layer not more than 5 Å in thickness. From this value, and from the charge density just quoted, it follows that the concentration of OH⁻ ions in the immediate vicinity of the polar group required to give this charge density will be about 0.45 molar. Thus to increase the concentration of OH⁻ ions in the vicinity of the polar groups it would be necessary to use bulk OH⁻ concentrations substantially greater than 0.45 molar. In other words, between *pH* 8 and *pH* 13 the concentration of hydroxyl ions in the vicinity of the polar groups remains constant, on the assumption that the mobility at *pH* 8 is due exclusively to OH⁻ ion adsorption.

Consequently, if this assumption were correct, it might be expected that the rate of hydrolysis of esters at the interface should remain unchanged between *pH* 8 and *pH* 13. But it is known that the rate of hydrolysis of esters at interfaces is a linear function of the OH⁻ ion concentration, and varies enormously between *pH* 8 and *pH* 13. Hence the assumption of specific adsorption of OH⁻ ions at *pH* 8 must be incorrect (unless, for some reason which is not clear to us, one is to assume that an OH⁻ ion adsorbed on an ester grouping at the surface is less capable of causing hydrolysis than one not specifically adsorbed on the ester grouping).

Incidentally, if any substantial degree of OH⁻ ion adsorption occurs, emulsification in unbuffered salt solutions should bring about a measurable *pH* change.

The charge density of 1.3×10^{13} electronic units still corresponds to only one anion adsorbed per 800 sq. Å, so that comparatively little lowering of interfacial tension would be produced due to the surface charge. This may be why Powney and Wood found comparatively little correlation between mobility and interfacial tension measurements.

Dr. A. J. Ham (*Liverpool*), in reply, said: The high mobilities noted for esters in the alkaline region are noted also for alcohols, while electro-osmotically carborundum surfaces have been found to possess an equally large negative charge.³ Hydrolysis cannot occur in the latter case, and OH⁻ adsorption provides the most general and simple explanation (see also reply to Dr. Danielli). Other factors do undoubtedly come into play in some cases, *e.g.*, Dickinson⁴ finds that iodide and thiocyanate ions are strongly adsorbed on cetyl acetate. This work on cetyl acetate is also of interest in that considerable correlation was possible between

¹ Williams, *Trans. Faraday Soc.*, 1940, **36**, 1042.

² Cf. Abramson, 1934, *Electrokinetic Phenomena* (New York), p. 110.

³ Hodgson, *unpublished work*.

⁴ Dickinson, *Trans. Faraday Soc.*, 1940, **36**, 839.

interfacial tension measurements and mobility, in contrast to Powney and Wood's work on paraffin chain salts.

Constancy of mobility above pH 8.0 (found for alcohols and esters) up to pH 11.90 is difficult to explain; no good alternative seems to present itself to our assumption of saturation with OH^- ions. It should be noted, however, that all our work is done at a constant cation concentration ($[Na^+] = 0.01 N$) in order to maintain approximate constancy of thickness of the double layer. If the cation concentrations were not controlled then constancy of mobility would not be found.

Dr. A. J. Ham (*Liverpool*), in reply to a member's question on Dickinson's paper, said: No calculation of the iso-electric point has as yet been attempted; it is found at approximately pH 2.3 in all cases recorded by Dickinson. The usual treatment would be complicated by the fact that one is dealing with adsorption on a charged surface.

On the Paper by Dr. Powney and Dr. Wood.

Dr. G. S. Hartley (*Winterslow*) said: I should like to point out that the formation of an atmosphere of paraffin-chain ions around an oil drop, without actual adsorption, is most improbable. There will be no potential energy advantage to the water molecules in bringing the paraffin chains near to the oil without actually pushing them into it. Nor would such a "remote" adsorption have no effect on interfacial tension. It would still be a "surface excess" in the sense of the Gibbs theory. If there is no change of tension with concentration, there can be no accumulation of salt either at or near the interface. Is it possible that the anomaly lies in undetected experimental error? The phenomenon occurs in extremely low concentration. Adsorption of a monolayer from a 0.001 % solution would require ions equivalent to the complete evacuation of solution up to about 0.2 mm. around the drop. No matter how slowly the drop is formed, it must break quickly. This has always seemed to the speaker a possible weakness of the drop volume method for very dilute solutions. The authors are to be congratulated on their examination of mobilities in these very dilute solutions. Could they, perhaps, with but little addition to the apparatus, examine sessile drops for change of form with change of concentration? Although quantitative measurements might not be possible, confirmation of the absence, if real, of any change would be obtained by a completely static method. Another possible explanation of apparent non-validity of the Gibbs equation may be that, in these dilute solutions, the concentration of ions in the water used is comparable with that added. The two-component form of Gibbs equation may not, therefore, be applicable.

Dr. R. K. Schofield (*Harpenden*) said: I do not see that there is any anomaly here. If these results are not vitiated by serious experimental error, they show us that ionic adsorption can influence the electrophoretic mobility at interfacial concentrations that are too low to have measurable effects on the interfacial tension. The interfacial concentrations for the higher bulk concentrations can be calculated from the interfacial tension data with the aid of the Gibbs equation. At low concentrations interfacial and bulk concentrations are substantially proportional to one another. Hence the very low interfacial concentrations corresponding to the electrophoretic mobilities can be approximately determined by extrapolation from the smallest values given by depression of interfacial tension.

Dr. A. D. B. Cassie (*Leeds*) said: If electrophoretic mobility is ascribed to adsorption of long-chain ions, one would expect it to be sensitive to changes of concentration at concentrations much lower than those required to give measurable changes of interfacial tension, because the ζ -potential must be built up at very low concentrations. The ζ -potential must correlate fairly closely with the potential ϕ discussed in the paper by Cassie

and Palmer, and equation (4) of their paper shows that ϕ will be independent of concentration when a surface equation of state of the form $FA = RT$ applies; if the equation is $FA = 3/2RT$ ϕ will change by roughly 10 milli-volts when A is halved. These calculations must necessarily be approximate because of the uncertainty regarding c_s , but they indicate that ϕ and the ζ -potential must acquire their large values almost as soon as adsorption occurs.

Dr. J. Powney and Dr. L. J. Wood (*London*), in reply, said: Observations on sessile oil drops as suggested by Hartley would certainly be of interest in connection with our results. In view of the calculations of Cassie and Palmer, it would appear at this stage that the most probable explanation of the observed anomalies is that high electrophoretic mobilities can arise from interfacial concentrations of long-chain ions so low as to be undetectable by normal methods of interfacial tension measurement.

On the Paper by Dr. Cassie and Mr. Palmer.

Dr. A. E. Alexander (*Cambridge*) said: Two small points on the first page may be possibly incorrect. Firstly, the lack of pronounced action of salts upon films of sodium docosyl sulphate¹ may have been due to traces of divalent cations already present in the substrate²; secondly, the increased capillary activity due to electrolytes with paraffin chain salts below the critical micelle concentration may be due to micelle formation and consequent removal of the time factor.³

The Chairman said: I would like to congratulate the authors on this paper. It covers a wide and important field and provides us with information of which many of us have been in need for some time.

Mr. R. C. Palmer (*Leeds*), in reply to Dr. A. E. Alexander, said: I agree that possibly the apparent increased capillary activity of cetyl sodium sulphate in the presence of NaCl recorded by Long, Nutting and Harkins, might be due to micelle formation having suppressed the slow change of surface tension with time: but the experiments of Powney and Addison could not be interpreted in this way. Powney and Addison give complete concentration/surface tension curves for various salt concentrations. If we take the kink in the curves as an indication of micelle formation then the lowering of S.T. by salt at detergent concentrations below the kink must mean greater adsorption.

On the Papers by Dr. King and Dr. Pink.

Dr. J. H. Schulman (*Cambridge*) said: It has been shown by Schulman and Cockbain,⁴ that in cases where the interfacial film is solid and neutral, emulsions of the type water in oil occur. These emulsions are consequently composed of irregular sacklets of water in oil of no regular size.

In cases where the interfacial film is composed of large molecules of paraffin ion compounds (either positive or negative) which consequently cause the interface to possess a charge, emulsions of oil in water will occur.

Removal of the diffuse layer by salts breaks the emulsion. If the salt also causes a solid molecular interlinked interface inversion of the emulsion occurs. If the interfacial film is both electrically charged and solid, oil in water emulsions exist of high viscosity.

Dr. G. S. Hartley (*Winterslow*) said: The speaker, while quite convinced by Pink's paper, pointed out that it was not really covered by

¹ Stenhagen, *Trans. Faraday Soc.*, 1940, **36**, 496.

² Langmuir and Waugh, *J.A.C.S.*, 1940, **62**, 2771.

³ Long, Nutting and Harkins, *ibid.*, 1937, **59**, 2197.

⁴ *Trans. Faraday Soc.*, 1940, **36**, 651.

its title, since the soaps which stabilise the emulsions concerned do so, and can only do so, it is considered, in a form *insoluble* in both water and oil. Of the many newer paraffin chain salts now well known, some have a very favourable partition between oil and water and would render possible an investigation of the subject of the title. I do not wish to disparage the author's motive in making the investigation described, or to deny its utility, but I would like to make a general plea for more work of this quality on emulsions to be made with the newer materials, which can be chosen so as to examine various factors separately without complication by others.

Dr. A. King (*London*) said: No data are available as to the droplet size of water in oil emulsions. Is it not probable that this may be large and that the tendency to cream which this emulsion type possesses may be due to this rather than to the electrical properties of the continuous phase?

Dr. A. J. Ham (*Liverpool*) said: King's conclusions with regard to the influence of the nature of the internal phase on the stability of emulsions may be compared with a few observations of Carruthers.¹ The latter also found that a small difference in density between continuous and disperse phases favoured stability. A second factor is the absolute size of the molecule of the internal phase, if this is too small then emulsions are unstable probably due to surface "end over end" rotation preventing OH⁻ ion adsorption. Carruthers did not use emulsifying agents, so that the criterion of difference in density appears to apply with or without such agents.

Dr. A. R. Martin (*London*) said: Hermann and I have arrived at conclusions² in many respects similar to those of King and his collaborators. When the salt of a bi- or higher valent metal added to an emulsion stabilised by sodium oleate was insufficient to react with all the sodium soap present, the volume of oil thrown out depended on the nature of the metal. If the electric charge on the droplets had been the chief factor determining the behaviour of the emulsion, these specific effects would have been related to the valency of the reacting kation (Schulze-Hardy rule). In fact, the influence of valency was slight and was sometimes overruled completely. We interpreted our results in terms of the extent to which the interfacial film of acid-soap was destroyed, the formation of sols of metal soap in the organic liquid peptised by oleic acid being an important factor in this connection.

A comparison of emulsions of paraffins and higher alcohols illustrates the interplay of some of the factors in emulsion stability, all of which hinge on the interfacial film. In a decyl alcohol emulsion the film was a composite one of sodium oleate and alcohol (*cf.* the work of Schulman and collaborators on molecular interaction in monolayers) and almost all the sodium oleate was adsorbed at the interface. Judged by persistence in time, high degree of dispersion and resistance to creaming this emulsion was more stable than a similarly prepared one of heptane, in which the interfacial film was acid-soap (1 Na-oleate—1 oleic acid) and in which the greater part of the soap remained in solution in the aqueous phase. However, on adding copper sulphate equivalent to one half the sodium oleate to each emulsion, about 80 % more oil separated from the decyl alcohol emulsion. By this test the coarser emulsion was the more stable. In the heptane emulsion the interfacial film had to some extent been maintained by the reserve of soap in the aqueous phase, which was lacking in the decyl alcohol emulsion.

If degree of dispersion does not determine emulsion stability, size-frequency analysis as a measure thereof must be used with caution. The oil-separation test for stability can be accelerated by centrifuging.

¹ Carruthers, *Trans. Faraday Soc.*, 1938, 34, 646.

² *Trans. Faraday Soc.*, 1941, 37, 25, 30.

Like Pink, Hermann and I found that magnesium oleate alone gave relatively stable W/O emulsions; other metal oleates (Zn, Ca, Ba, Cu, Al and Th) either gave very unstable W/O emulsions or none at all. Some of these oleates (Cu, Al) are easily peptised in the oil phase by oleic acid, and zinc oleate is soluble in (wet) benzene. Addition of a Mg salt to an emulsion stabilised by sodium oleate was exceptional in producing in the separated water a thick suspension of magnesium oleate, apparently stabilised by $\text{Mg}(\text{OH})_2$. It was this suspension which, on shaking, stabilised a W/O emulsion. It appears that as emulsifying agents for W/O emulsions "metal soaps" are restricted in number and must be classed with the finely divided solids.

Dr. A. King (*London*), in reply to a question by Frazer, said: Creaming of an emulsion is the gravity separation of the dispersed liquid droplets which results in the appearance of a separate layer of *continuous phase* liquid. When an emulsion *breaks* the dispersed droplets coalesce to form a layer of free disperse phase liquid. In the former case the emulsion is easily reconstituted as a homogenous system by gentle shaking, in the latter case more energetic treatment is required to redisperse the separated liquid while in many instances broken emulsions cannot be re-formed at all.

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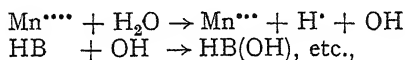
14 JUL 1941

KINETICS OF THE OXIDATION OF ORGANIC COMPOUNDS BY POTASSIUM PERMANGANATE. III. FORMIC ACID.

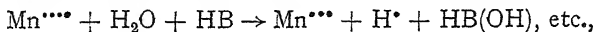
BY D. R. MANN AND F. C. TOMPKINS.

Received 21st October, 1940.

In the first two papers of this series,^{1, 2} it was concluded that the oxidation of the 2:6-dinitrophenol molecule proceeded by the two consecutive reactions:



to products, where HB represents the dinitrophenol molecule. The possibility of ternary collisions with a solvent molecule,



was not necessarily excluded. This theory was thus not at variance with those of Fales and Roller,³ Launer and Yost,⁴ and Launer,⁵ all of whom concluded that the Mn^{VII} ion was chiefly responsible for the oxidations. It thus appeared that the same type of mechanism was operative in all types of permanganate oxidations.

The oxidation of formic acid appeared the most suitable for investigation, since (a) intermediate oxidation products, except the performate ion, are not expected; (b) there is no evidence available which suggests the possible formation of any tri- or tetra-manganic formate ion similar to that found in the oxidation of oxalic acid. Holluta^{6, 7, 8, 9} found that the formate ion is the potent reducing agent in this reaction, which is approximately of the second order, but there were certain disturbances which were greatest at the start of the reaction in acid concentrations greater than 0.001 N. His results are confirmed and extended in the present work. His suggested mechanism for the oxidation is open to criticism, and involves intermediate rate equations of high and improbable order. Hatcher and West¹⁰ found that the rate varies inversely with the hydrogen-ion concentration which they derive from different acids, and that formic acid appears frequently as an oxidation intermediate product in the reaction of more complex aliphatic acids with

¹ Alexander and Tompkins, *Trans. Faraday Soc.*, 1939, **35**, 1156.

² Alexander and Tompkins, *J. South African Chem. Inst.*, 1940, **23** (2), 1.

³ Fales and Roller, *J.A.C.S.*, 1929, **51**, 345.

⁴ Launer and Yost, *ibid.*, 1934, **56**, 2571.

⁵ Launer, *ibid.*, 1932, **54**, 2597.

⁶ Holluta, *Z. physik. Chem.*, 1922, **101**, 34.

⁷ *Ibid.*, 489.

⁸ *Ibid.*, 32.

⁹ *Ibid.*, 276; 1925, **115**, 137.

¹⁰ Hatcher and West, *Trans. Roy. Soc. (3)*, 1927, **21** (3), 269.

permanganate, and hence a complete study of the formic acid oxidation must be a necessary preliminary to that of these more complex oxidations.

Experimental.

The procedure adopted was similar to that previously used. The idometric method has been preferred throughout, since we were unable to obtain reproducible rate curves using the gasometric method of Launer.⁵ Both Kahlbaum's and A.R. 90 % formic acid were used—no difference in rates were observed with the two products. All other reagents were of A.R. quality. The normality of the solution with respect to sulphuric acid was always less than that required to allow the permanganate to react $2\text{MnO}_4' + 6\text{H}^+ \rightarrow 2\text{Mn}^{++} + 3\text{H}_2\text{O} + 5\text{O}$ —details of procedure have already been given.¹ The formate ion reacts quantitatively according to the equation, $2\text{KMnO}_4 + 3\text{HCOOK} \rightarrow \text{KHCO}_3 + 2\text{K}_2\text{CO}_3 + 2\text{MnO}_2 + \text{H}_2\text{O}$, in the presence of alkali carbonate, and may, in fact, be estimated in this manner.¹¹ We have preferred to standardise the formic acid by direct titration with standard barium hydroxide solutions using phenolphthalein, since there is the danger of oxidation of it by the freshly formed MnO_2 .

The three main inaccuracies here in the idometric method are (a) volatilisation of iodine, (b) the photochemical reaction of unchanged formic acid with the liberated iodine during titration with thiosulphate, (c) the photochemical autooxidation of hydriodic acid in higher acid concentrations. These are negligible if (a) the acid strength is maintained at a minimum, (b) a large excess of potassium iodide is added to keep most of the iodine liberated in the form of the triiodide ion, (c) a known volume of standard thiosulphate is quickly added after the oxidation is arrested by the addition of acidified KI, so that the iodine remaining was always less than 0.5 c.c. $\text{N}/10$, and (d) diffuse light is used throughout.

The pH of the solutions was determined throughout the reaction, using

a glass electrode in conjunction with a Cambridge electrometric valve pH meter and the initial values at zero time were obtained by extrapolation.

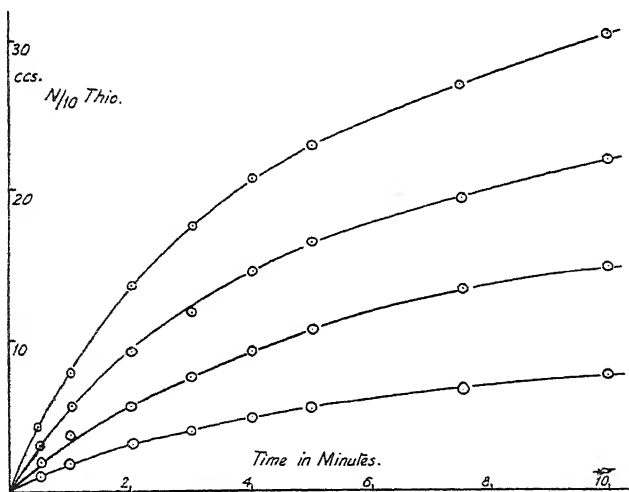


FIG. 1.

Results.

Preliminary experiments showed that the rate was accelerated by the addition of neutral salts, and hence

throughout any of the series the total ionic strength was maintained constant by the addition of a suitable volume of an ammonium sulphate solution.

¹¹ Vogel, *Quantitative Inorganic Analysis*, 1939, 361.

Series A.—Temp. 30.01° C. Total ionic strength, 0.1026. Total vol., 120 c.c. KMnO_4 , 0.0025–0.01 M. Formic acid, 0.226 M. Sulphuric acid, 0.0438 M. Formate ion concentration initially: 1.067×10^{-3} g. ions/l.

Fig. 1 shows the plot of the loss of oxidising power of KMnO_4 in terms of c.c. N/10 thiosulphate against time in mins. There is no induction period. Table I, which is self-explanatory, shows that the rate is proportional to the KMnO_4 concentration—a general conclusion for all oxidations so far investigated.

TABLE I.

Curve No.	1	2	3	4
Conc. KMnO_4 in g. mol./l.	0.0100	0.0075	0.0050	0.0025
Init. vel. in c.c. N/10 thio./min.	7.76	5.82	3.90	1.92
Vel./conc. KMnO_4	776	776	780	768

Series B.—Temp. 30.01° C. Ionic str., 0.0859. Total vol., 120 c.c. H_2SO_4 , 0–0.0167 M. Formic acid, 0.025 M. KMnO_4 , 0.00833 M. The results are collected together in Table II. The formate ion concentrations are calculated from the $p\text{H}$ values, using the value of 1.768×10^{-4} for the dissociation constant of formic acid.¹² The last row in the table shows

TABLE II.

Time in Min.	c.c. N/10 Thiosulphate.				
1/2	8.0	5.81	4.78	3.04	0.98
1	14.83	11.34	9.07	6.00	1.74
2	23.21	19.71	15.12	9.98	3.03
3	27.96	25.40	19.84	13.00	3.97
4	29.60	28.15	23.59	15.95	4.74
5	29.90	29.51	26.59	18.78	5.00
Conc. H_2SO_4 in g. mol. per litre $\times 10^4$	0.00	8.33	41.65	83.33	33.33
Initial $p\text{H}$	2.79	2.65	2.48	2.27	1.69
Conc. formate ion in g. ions/l. $\times 10^3$	98.2	73.1	50.8	31.8	8.56
Initial vel. in cc. N/10 thio. per min.	24.8	17.6	12.5	7.95	2.15
Vel./conc. formate ions $\times 10^{-2}$	2.52	2.41	2.47	2.49	2.49

that the reaction is of the first order with respect to the formate ion, and hence the sulphuric acid plays no part in the oxidation except in regulating the formate ion concentration.

Series C.—Temp. 30.01° C. Ionic strength, 0.1000. Total vol., 120 c.c. Formic acid, 0.004165–0.075 M. Sulphuric acid, 0.004165 M. KMnO_4 , 0.00833 M. (Table III).

Table III shows that the conclusion above is confirmed over an 18-fold variation in the formate ion concentration—there is no retardation at higher concentrations of this ion. The reaction thus appears to be kinetically of the second order. The familiar expression

$$k = \frac{2.303}{i(a-b)} \cdot \log_{10} \frac{T_i(T_0 - T_\infty)}{T_0(T_i - T_\infty)},$$

cannot, however, be used directly in the calculation of the velocity constant, since as the oxidation proceeds there is a loss in hydrogen ions

¹² Harned and Embree, *J.A.C.S.*, 1934, 56, 1042.

which causes the degree of dissociation of the formic acid to vary with time. The formate ion concentration, however, may be calculated at any time from the pH of the solution, and the loss in oxidising power of the

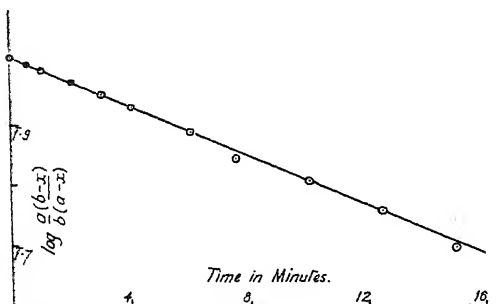


FIG. 2.

$KMnO_4$ as reflected in the thiosulphate titration. In Fig. 2 the logarithmic term above is plotted, using the calculated formate ion concentration, against time in mins., and it confirms the bimolecular character of the reaction.

Series D.—Temp. $20.25^\circ C$. Total vol., 120 c.c. Total ionic strength varying from 0.0300 to 0.1862 by the addition of ammonium

sulphate. Formic acid, 0.025 M. $KMnO_4$, 0.005 M.

It was necessary to determine the pH values as usual, since the variation in ionic strength not only affected the rate of oxidation, but also the formate ion concentration. The results are collected together in Table IV.

TABLE III.

Time in Min.	c.c. N/10 Thiosulphate.					
1	10.12	9.00	7.48	5.70	3.92	1.38
2	16.00	15.03	12.96	6.65	6.68	2.63
3	20.31	19.89	17.10	13.10	9.07	3.63
4	23.30	22.53	20.30	16.00	11.22	4.36
5	26.25	25.60	23.30	18.30	12.25	5.23
7½	29.84	29.00	27.45	22.88	16.30	6.18
10	31.20	30.73	29.20	25.81	18.96	7.30
Conc. formic acid in g. mol./l.	0.075	0.05	0.0333	0.02082	0.01249	0.00416
Initial pH	2.16	2.25	2.28	2.33	2.36	2.39
Conc. formate ion in g. ions/l. $\times 10^4$	18.61	15.25	10.82	7.37	4.84	1.73
Vel. in c.c. N/10 thio. per min.	13.5	11.2	7.85	5.55	3.61	1.26
Vel./conc. formate ion	72.5	73.5	72.6	74.6	74.5	72.8

TABLE IV.

Time in Min.	c.c. N/10 Thiosulphate.				
1	3.00	3.94	4.39	5.24	6.48
2	5.38	6.65	7.50	8.80	10.51
3	7.50	9.04	10.06	11.42	13.12
4	9.45	11.20	12.18	13.42	14.92
5	11.24	12.94	13.89	15.06	16.23
7½	14.76	15.97	16.82	17.34	17.80
Total ionic strength	0.0300	0.04953	0.06904	0.1081	0.1862
Initial pH	2.68	2.74	2.78	2.81	2.86
Formate ion conc. in g. ions/l. $\times 10^3$	1.784	1.996	2.157	2.281	2.499
Vel. const. in g. equ. ions/l.	25.7	29.6	32.2	38.0	45.9

The variation of $[\log_{10} k - \log_{10} k_0]$, where k_0 is the extrapolated value of the velocity constant at zero ionic strength, with the square root of the ionic strength gives a plot showing a slight curvature, since the ionic strengths are higher than those to which the Debye-Huckel equation is applicable. The limiting slope is quite clearly defined, however, and has a value of 1.06, and is positive. This indicates that the reaction is between two univalent similarly charged ions, *e.g.* the $\text{H} \cdot \text{COO}'$ and the MnO_4' ions.

Series E.—Temp., 30.01° C. Total vol., 120 c.c. Formic acid, 0.0416 M. KMnO_4 , 0.00833 M. Sulphuric acid, 0.0167 M. MnSO_4 , 0.00168 M. (Table V).

TABLE V.

Time in Sec.	c.c. N/10 Thiosulphate.				
15	1.24	1.23	1.20	1.18	1.10
30	1.70	1.62	1.56	1.45	1.30
45	2.16	2.01	1.89	1.70	1.51
60	2.63	2.41	2.21	1.95	1.73
Conc. MnSO_4 in g. mol. per l. × 10 ³	0.00	2.80	5.60	11.20	16.80
Vel. in c.c. N/10 thio. per min.	1.86	1.58	1.30	1.00	0.86
$1/v - 1/v_0$	—	0.105	0.232	0.463	0.625
$(1/v - 1/v_0)/\text{conc. MnSO}_4$	—	37.5	41.4	41.3	37.2

In the above, v represents the velocity of the reaction in presence of MnSO_4 , and v_0 is the velocity without the addition of MnSO_4 . The plots of these figures are coincident over the first ten seconds, and then become linear. The slope of the linear portion is that referred to in the table, and this falls with increasing MnSO_4 . It will be seen that Mn^{++} has not its usual acceleratory effect, but retards approximately in proportion to the amount present for constant KMnO_4 . This is discussed later.

Series F.—Temp., 30.18° C. Total ionic strength, 0.2000 KMnO_4 , 0.00833 M. Formic acid, 0.0417 M. Sulphuric acid, 0.0166 M. Potassium fluoride, 0.00718 M.

The addition of fluoride ions normally causes a retardation in permanganate oxidations,^{1, 2, 3, 5} but Holluta⁹ showed that it accelerated the formate ion oxidation. This is confirmed here, but is due to the effect of the KF on the dissociation of the formic acid, and not due to the formation of complexes with intermediate Mn ions. From the last row it is

TABLE VI.

Time in Min.	c.c. N/10 Thiosulphate.				
1/2	2.00	3.28	5.60	10.02	21.00
1	3.87	6.09	10.08	17.00	26.90
2	7.47	10.82	17.40	24.30	32.21
3	10.30	14.76	21.92	27.58	33.80
4	12.57	17.87	24.83	29.37	34.50
5	14.28	20.28	26.69	30.47	34.80
KF in g. mol./l. × 10 ²	1.433	1.433	2.867	4.301	7.165
Vel. in c.c. N/10 thio. per min.	3.60	6.20	12.00	24.00	43.10
Initial pH	1.88	2.14	2.44	2.76	3.15
Formate ion. conc. in g. ions/l. × 10 ⁴	5.52	9.95	19.4	38.6	65.3
Vel./formate ion conc. × 10 ³	6.52	6.23	6.21	5.70	6.60

seen that when the effect of the KF on the dissociation of the formic acid is taken into account, the presence of this salt scarcely effects the rate, despite the fact that in the highest concentration of KF there is ten times more than that of permanganate itself. The constancy in this last row is not good, since the pH values showed a pronounced drift, presumably due to the attack by KF in presence of sulphuric acid on the glass membrane. The conclusion, however, is clear.

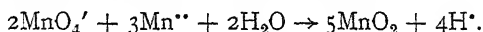
Series G.—Total ionic strength, 0.0875. Total vol., 120 c.c. Sulphuric acid, 0.004167 M in I, II, III, below :—

- | | |
|-----------------------------|--------------------------------|
| I. Formic acid, 0.04167 M. | KMnO ₄ , 0.00833 M. |
| II. Formic acid, 0.04167 M. | KMnO ₄ , 0.00150 M. |
| III. Formic acid, 0.0250 M. | KMnO ₄ , 0.00833 M. |

Temperatures, 15.80, 23.10, 30.18, 37.68° C. for I, II, and III. Using the three solutions (I, II, III), velocity constants were obtained at the four temperatures, and from these the heat of activation was calculated in the usual manner. Since these results show no new features of interest, the table is omitted. The average value for the heat of activation energy is 11,200 cal., and is to be compared with that which may be calculated from Holluta's results in the same region of temperature (10,700 cal.), but at higher ionic strengths.

Discussion.

The present results confirm the experimental work of Holluta—the formate ion is oxidised, the reaction is kinetically of the second order, there is no induction period. As in other oxidations,^{1, 5, 13} the sulphuric acid merely has a secondary electrolytic effect in low concentrations. The primary electrolytic effect, which was not studied by Holluta, shows that the rate determining process is a bimolecular collision between the formate ion and a singly charged negative ion, which has been identified as the MnO₄'. Confirmation of the nature of this second reactant is afforded by the results obtained on the addition of Mn⁺⁺ and F' ions. The former react with MnO₄' ions according to



The reaction has an induction period^{14, 15} which is lengthened by the addition of sulphuric acid, and the rate is approximately proportional to the concentration of Mn⁺⁺ ions, according to some preliminary results which we have obtained on this reaction. The addition of such ions in the formic acid oxidation should therefore have initially little effect on the rate, but should cause a subsequent reduction in rate by the removal of MnO₄' in proportion to the amount added. This has been found (Table V); hence MnO₄' ions is the other reactant and, moreover, it suggests that intermediate ions (Mn⁺⁺⁺ and Mn⁺⁺⁺⁺) play little part in the reaction.

The acceleration caused by the addition of KF found by Holluta, and confirmed here, led the former to believe that all complex-forming anions should have the same effect, thereby invalidating the conclusions of Schilow¹⁶ and Launer. The acceleration, however, is solely due to the increasing dissociation of formic acid in the presence of this salt, and when a correction is applied it is found that the rate is scarcely affected

¹³ Musgrave and Moelwyn-Hughes, *Trans. Faraday Soc.*, 1933, 29, 1162.

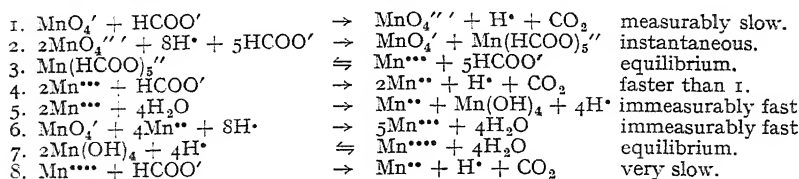
¹⁴ Polissar, *J. Chem. Ed.*, 1936, 13, 40; *J. Physic. Chem.*, 1935, 39, 1057.

¹⁵ Bradley and Van Praagh, *J.C.S.*, 1938, 1624.

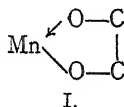
¹⁶ Schilow, *Ber.*, 1903, 36, 2735.

(and, in fact, may be slightly reduced) when fluorine ions are present. Since these ions virtually remove Mn^{+++} ions by forming MnF_4' ions, it confirms the conclusion above that Mn^{+++} ions are either absent or do no oxidising work—a fact which Holluta deduced from his other experimental data.

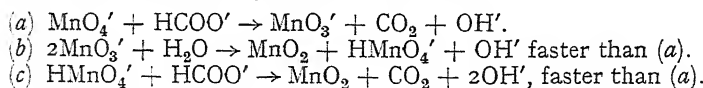
The mechanism suggested by Holluta is as follows:—



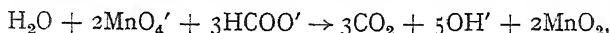
It is similar in its main features to that suggested by Launer for the oxidation of oxalic acid, and centres around the possibility of complex formation in 2. Weinland and Stark¹⁷ have reported the complex salt of formula $Mn_3(HCOO)_6(HCOO)_3 \cdot 2H_2O$, which is quickly decomposed by water but may be prepared by the action of 90 % formic acid on MnO_2 in the cold. We have not been able to confirm this, although a slow oxidation of the acid by MnO_2 has been found. All complexes so far prepared with the Mn^{+++} ion, *e.g.* oxalates,¹⁸ malonates,¹⁹ tartrates, racemates and citrates,²⁰ hydroxyacids,²¹ and salicylates,²² are chelate compounds in which the structure (I) is common to all. From structural considerations a complex of this type would be impossible with the formate ion, although one with the associated molecule $(HCOOH)_2$ appears possible. No proof of the existence of the ion $Mn(HCOO)_5''$ is given by Holluta, and there is no evidence in the present results to suggest its presence. Equation 4 may be eliminated, since it has been shown that the Mn^{+++} ions do little oxidation, and, moreover, since reaction 6 is measurably fast and reaction 4 is stated to be faster than reaction 1, then the addition of Mn^{++} ions by reaction 6 would yield an increase concentration of Mn^{+++} ions, and hence cause an acceleration. In the same way, there should be an initial induction period, and fluorine ions should cause a marked retardation. Reaction 8 has been confirmed, but is very slow, and is negligible, as may be deduced from the method of estimating formates previously mentioned.¹¹



The present results suggest the mechanism:—



The rate-determining process is thus the bimolecular collision of $H \cdot COO'$ and MnO_4' and the three equations lead to the stoichiometrical equation



which thus proceeds without change in ionic strength. The possibility of a ternary collision of the two ions with a molecule of water may be

¹⁷ Weinland and Stark, *Ber. B.*, 1926, **59**, 471.

¹⁸ Cartledge and Ericks, *J.A.C.S.*, 1936, **58**, 2061.

¹⁹ Meyer and Schramm, *Z. anorg. Chem.*, 1922, **123**, 56.

²⁰ Pickering, *J.C.S.*, 1916, 235.

²¹ Verkade, *Chem. Weekblad*, 1917, **14**, 420.

²² Barbieri, *Ber. B.*, 1927, **60**, 2421.

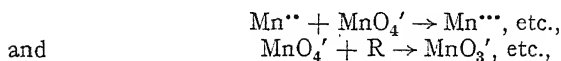
eliminated by a consideration of the molecular statistics of the reaction, using the theoretical expression for the bimolecular constant

$$k = \frac{N}{1000} \sigma_{12}^2 [8\pi RT (1/M_1 + 1/M_2)]^{1/2} \cdot e^{-E/RT}$$

taking a value of 5×10^{-8} for the average diameter of the ions, and $M_1 = 46$ and $M_2 = 119$, where k is in g. mol./l. per sec. at zero ionic strength. The agreement of calculated and experimental values (2.4 and 1.3) is as good as may be expected.

In the reaction (a) the intermediate formation of the performate ion HCOO' which undergoes an intramolecular change to the HCO_3' is not excluded—we rather incline to the view that a “complex” is formed between the two ions in which a co-ordinated oxygen atom in the MnO_4' donates an electron pair to the hydrogen atom of the formate ion, forming a “hydrogen bridge”—this then breaks at the C—H bond. Intermediate formation of manganites MMnO_3 , where M is a univalent cation, has been proved in the thermal decompositions of permanganates,²³ and the kinetics of the decomposition of the silver salt, which is an autocatalytic reaction, are adequately interpreted in terms of the intermediate²⁴ AgMnO_3 . Reaction (b) takes into account the well-known mutual oxidation and reduction common to manganites. In the oxidation of unsaturated hydrocarbons, Nametkin²⁵ has adduced a certain amount of evidence to show that the compound KHMnO_4 is formed during the reaction.

The oxidation of formic acid is different from that of the three other oxidations which had been studied in detail. Although these latter differ widely in character, e.g. that of oxalic acid being the oxidation of an anion, that of nitrophenol being the oxidation of a complex aromatic molecule, and that of chrome alum being the oxidation of a cation to an anion (CrO_4'), they display similar characteristics, such as having an induction period, being catalysed by Mn^{++} ions and retarded by F' ions, and in that complex formation with the Mn^{+++} ion is possible. This is explained in terms of the ultimate production of Mn^{++++} ions which are responsible, directly or indirectly, for the oxidation. It is also of interest to note in such oxidations that the activation energy is higher (dinitrophenol 14,400 cal., *m*-dinitrobenzene 15,300 cal.,²⁶ 2:4-dinitrobenzene 17,300 cal.²⁶) than those oxidations in which there is no induction period (formic acid 11,200 cal., picric acid 12,200 cal., benzoic acid 12,700 cal.²⁶). The reaction mechanism thus appears to depend on the relative probability of the two reactions



where R is the reducing agent. It is suggested that the second is favoured when R contains a mobile hydrogen atom, as in the formate ion—consequently it would be anticipated that the oxidation of phenol by KMnO_4 would be rapid and have no induction period. There is some evidence supporting this.²⁷ The other feature in common is that in all oxidations where the Mn^{++++} is chiefly responsible, complex formation has been found.

²³ Holluta, *Z. physik. Chem.*, 1925, **115**, 143.

²⁴ Sieverts and Theberath, *ibid.*, 1922, **100**, 463.

²⁵ Nametkin, *J. Russ. Phys. Chem. Soc.*, 1924, **55**, 70.

²⁶ Hinshelwood, *J.C.S.*, 1919, 1188; 1936, 368.

This may be an essential condition, since such a complex acts as a reservoir for Mn^{+++} ions, and thus prevents their ultimate hydrolysis to MnO_2 without loss in oxidising power. Further than this cannot be said at the present, since the number of oxidations which have been thoroughly investigated are few, and so little is known about the Mn^{++}/MnO_4' reaction. The work is being continued.

Summary.

The oxidation of formic acid by $KMnO_4$ in aqueous solutions of low acidity has been studied kinetically. The mechanism is completely different from that found with dinitrophenol—reasons are suggested in explanation, and a mechanism of the reaction given. The reaction is kinetically of the second order, and has a heat of activation of 11,200 cal.

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CRYSTALLISATION IN SILICATE SLAGS AND GLASSES.

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Crystallisation, and especially the crystallisation and structure of eutectics, has long been a subject of study by metallurgists who have been concerned primarily with crystal growth and changes in eutectic structure, brought about by different heat treatments. The rapidity with which crystallisation takes place in such fluid media as molten metals and alloys gives rise to extremely fine eutectic structures, and there is often a tendency to regard such structures as the unique forms of particular eutectics and to forget that the separation of an eutectic or eutectoid is simply the simultaneous crystallisation of solid phases which have reached the limit of solubility in the liquid condition or in solid solution. For in general if a section of such a eutectic mixture be etched, there will be no recognisable traces of regular crystalline orientation, and a strongly crystalline metal such as antimony or bismuth is apt to impress its own form on a eutectic of which it is a constituent, as for example in the bismuth-tin system. The lead-tin system is an excellent example of the fine structure of metal eutectics, and metallurgists the world over are familiar with the examples of the fine lamellar structure of eutectoid pearlite in the iron-carbon system given in the photomicrographs at 5000 and 8000 diameters by Hadfield and Elliott¹ at this Society's General Discussion on "The Microscope, Its Design, Construction, and Application."

One purpose of this paper in addition to reporting the crystallisation relationships encountered in a highly viscous medium, such as a commercial soda-lime-silica glass, is to show that in the binary eutectic range of such materials the individual crystalline characteristics of

¹ *Trans. Faraday Soc.*, 1920-21, 16, 161.

each phase are retained, in contrast to the observed and more widely known character of eutectic separation in metals.

The crystallisation of primary phases and eutectics is a subject of great importance in the science of mineralogy and in the technology of slags, glasses and all fused silicates. For many years the only work on the subject was the classical researches of Vogt² who investigated the crystalline constitution of many slags, and observed the order of separation of the different crystalline phases. In a further General Discussion of the Faraday Society on the "Physical Chemistry of Igneous Rock Formation" the subject of crystallisation and eutectic separation in silicate systems received some consideration, mainly by Desch³ and Hallimond,⁴ but it was apparent that compared with metallography progress in this field was extremely slow. Indeed, it has continued to be so. This is due to the nature of the materials investigated, the greater difficulties of identification of mineral constituents, and the fact that the equilibrium diagram of many silicate systems is not quite so useful as in metallurgy since natural silicate systems so rarely attain equilibrium.⁵

Heterogeneous Equilibrium in Silicate Systems.

The last generation has paid increased attention to silicate equilibria, and the results obtained have been of great value in the advancement of knowledge in the related sciences of ceramics, refractory materials, and glass technology, which latter may be regarded as including technical slags from industrial furnaces. The Geophysical Laboratory, Washington, D.C., U.S.A.,⁶ has played a major part in the study and publication of these equilibrium diagrams, and data of this type for the many systems of importance in the above-mentioned industries have been collected together by Hall and Insley.⁷

Much less attention has been given, however, to the study of the rates of crystallisation of silicate melts. Whilst the equilibrium diagram studies have already shown the closeness of the phase relationships in many silicate systems to those long known in the case of the equilibrium diagrams of metal systems, crystallisation studies emphasise still further these relationships and show that the differences observed are of degree only and controlled by the physical conditions of the crystallisation process. Indeed, technical silicate glasses appear in many ways to be ideal materials for the study of crystallisation, which, in such media, takes place only slowly on account of the high viscosity of the glasses, as opposed to the crystallisation of metals which by comparison is almost instantaneous. The subject is of special importance in glass technology since the appearance of crystallisation, or devitrification, means the destruction of the glassy state. Accordingly, the very few published researches⁸ on crystal growth in silicate

² *Die Silikatschmelzungen*, Christiania (Oslo), J. Dybwad, 1903-4, 2 vols.

³ *Trans. Faraday Soc.*, 1924-5, **20**, 469.

⁴ *Ibid.*, 1924-5, **20**, 489.

⁵ See discussion by N. L. Bowen on paper by Desch, *loc cit.*³

⁶ For a complete list of such publications see Morey, *J. Soc. Glass Tech.*, 1936, **20**, 245.

⁷ *J. Amer. Ceram. Soc.*, 1933, **16**, 455-567; 1938, **21**, 113-64. In all 332 phase rule diagrams are collected together in this work.

⁸ Zschimmer and Dietzel, *Sprechsaal*, 1927, **60**, 110, 129, 165, 186 and 204. Zschimmer, *J. Soc. Glass Tech.*, 1929, **13**, 76. Parmelee and Monack, *ibid.*, 1929, **13**, 322. Littleton, *ibid.*, 1931, **15**, 262.

systems have been concerned with glasses, and it is a purpose of this paper to discuss the results obtained in the light of the equilibrium diagram and the known high viscosity of glass.

Thus, whilst there is now available a store of knowledge regarding the equilibrium conditions of silicate systems, there is as yet little information on the rate of attainment of equilibrium in these systems, and it is true to say that such information is vitally important in the glass, refractory, and ceramic industries.

The Measurement of Crystallisation Velocity.

To determine the rate of crystal growth in glasses the writer has employed a method due originally to Tammann⁹ and later employed by Ponomareff,¹⁰ Sawai and Kubo,¹¹ and by Silverman¹² for the determination of liquidus temperatures. Considerable improvements have been effected and the technique has been described elsewhere¹³ under the title of the gradient method. Briefly the method consists in heating a sample of the homogeneous glass sufficient to give a layer of glass 1-2 mm. in depth in a platinum-5 per cent. rhodium boat six inches long and half an inch in width in a gradient electric furnace. The gradient is such that from the inner end of the boat the temperature falls approximately 25-30° C. an inch, and this gradient has been found quite suitable both for crystal growth measurements along the boat at different positions, the temperatures at which are determined by the known gradient, and for liquidus temperature determinations.¹⁴ The liquidus temperature corresponds to the boundary between glass and glass + crystals. The temperature gradient existing along the boat is measured by means of a platinum-platinum rhodium thermocouple caused to travel underneath the boat in contact with the under surface, the boat being suitably supported on a refractory sillimanite carrier. To obtain a photomicrographic record of the results the devitrified specimen is removed from the boat, a process usually effected without difficulty, and photographs taken at known intervals along the specimen.

Crystallisation-Temperature-Time Relationships.

The form of the crystallisation-temperature relationships for super-cooled solutions, than which for glasses there is as yet no better definition, was first indicated by Tammann¹⁵ and is given by a curve of the type illustrated in Fig. 1. In general, there is a temperature of maximum crystal growth characteristic of each composition. This temperature is always lower than the liquidus temperature, and in glasses may be as much as 150-200° below the liquidus. The temperature of maximum crystallisation velocity, T_M , results from two forces which mutually oppose each other. They are, the "crystallising force" which increases with progressive lowering of the temperature below the liquidus temperature, and the "resistance to crystallisation" which also increases with lowering of the temperature below the liquidus and comprises the

⁹ *Z. anorg. Chem.*, 1914, **87**, 248; *J. Soc. Glass Tech.*, 1925, **9**, 166.

¹⁰ *Z. anorg. Chem.*, 1914, **89**, 383; *J. Soc. Glass Tech.*, 1927, **11**, 39.

¹¹ *Ibid.*, 1937, **21**, 113.

¹² *J. Amer. Ceram. Soc.*, 1939, **22**, 378.

¹³ Preston, *J. Soc. Glass Tech.*, 1940, **24**, 101.

¹⁴ The liquidus surface of portions of a system could be determined by this means with fair rapidity though not so accurately as by the more laborious classical quenching method.

¹⁵ *Kristallisieren und Schmelzen*, Leipzig, J. A. Barth, 1903. *Der Glaszustand* Leipzig, L. Voss, 1933.

viscosity of the liquid and the rate of diffusion of the crystal components through the liquid.

The treatment which follows in the next three sections is entirely novel. The crystallisation-temperature relationships have been derived by a method fundamentally different from that of Tammann and which has been favourably commented on by Morey of the Geophysical Laboratory.¹⁶

Crystallisation-temperature curves obtained by the writer for a sheet glass composition, the liquidus temperature of which had been determined as 965°, are shown in Fig. 1. It is at once obvious from these curves that crystallisation does not proceed at a linear rate, and the reporting of crystal growth in such viscous liquids as so many millimetres per hour has little significance unless the total time of heating

be known and stated. In the present case it may be shown by plotting the data contained in Fig. 1, that crystal growth is approximately linear up to a total heating period of one hour, beyond which the rate of crystal growth gradually decreases, and even at the end of 50 hours the average crystal size is only about twice that found at the end of the one-hour period. There are two chief reasons for this. Below T_M diffusion of essential components towards the crystal becomes increasingly difficult, whilst above T_M saturation may be reached and no further crystal growth be possible owing to the fact that equilibrium conditions have actually been established in this region.

To appreciate fully the form of the crystallisation-temperature curves it is necessary, in the writer's view, to correlate them with the equilibrium diagram for the particular system

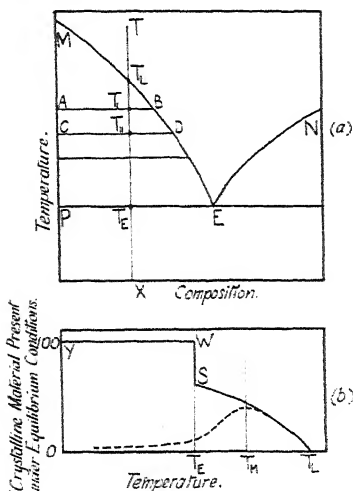


FIG. 1.—Relationships between proportions of crystalline material present under equilibrium conditions deducible from the equilibrium diagram.

and to consider the proportion of crystalline phase present rather than crystal size or rate of growth.

Crystallisation and the Equilibrium Diagram.

Consider an ideal binary eutectiferous system such as shown in Fig. 2. From the proportions of crystalline and liquid phases present at different temperatures for a composition such as X, a curve may be constructed showing the percentage of crystalline material present under equilibrium conditions, and this has been done in Fig. 2b. The right-hand portion of this curve is derived by simple geometrical construction from the liquidus curve of the equilibrium diagram, and covers the temperature range from the liquidus temperature of the composition under investigation to the binary eutectic temperature.

¹⁶ Private communication.

Below the eutectic temperature the composition consists of 100 per cent. crystalline material. A similar curve for a ternary system may readily be constructed if the equilibrium diagram be known, and it will consist of two curved portions corresponding to the separation of primary phase between liquidus and binary eutectic temperatures, and to the separation of binary eutectic between the temperatures of first appearance of binary eutectic and the ternary eutectic, and a straight portion at 100 per cent. crystalline material below the ternary eutectic temperature.

For viscous undercooled liquids such as glasses the complete crystallisation curves are rarely realised, and in general, before even the binary eutectic temperature is reached, the effects of greatly increased viscosity and difficulties of diffusion at lower temperatures results in gradually decreasing rates of crystal growth, and we obtain crystallisation curves of the type shown by the broken line in Fig. 2b.

In crystal growth measurements of the glass of percentage composition 72.15 SiO_2 , 2.02 R_2O_5 , 8.91 CaO , 2.05 MgO , 13.58 Na_2O and 0.73 K_2O ,¹⁷ for which results have been given in Fig. 1, certain features were observed which are of general interest to the subject of crystallisation, and especially that of eutectic separation, and which are illustrated in Figs. 4 to 9.

A perspective drawing of that portion of the soda-lime-silica diagram of importance in the study of commercial glass compositions is given in Fig. 3, and has been constructed by the writer from the two dimensional diagram of Morey¹⁸ of the liquidus surface of this system, no previous attempt having been made to indicate the phase boundary surfaces below the liquidus surface. Although the glass examined is not a pure soda-lime-silica glass its composition approximates sufficiently to that of a simple three-component glass that the processes of crystallisation occurring may be illustrated by reference to the equilibrium model and are typified by the composition Y. The liquidus temperature for this glass was 965° , and the temperature of maximum crystal growth 910° . The primary crystalline phase in this composition is devitrite,¹⁹ $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$, and the devitrite-silica binary eutectic first appears at 850° . From the equilibrium diagram it is seen that this eutectic should consist of devitrite and quartz. The stability relationships of silica, however, are very ill-defined,²⁰ and frequently cristobalite and tridymite, the high temperature forms of silica, co-exist together and persist as pseudo-stable phases at lower temperatures instead of the more difficultly attainable quartz. The form which this eutectic takes is shown in Fig. 4, and it is seen that each crystalline phase retains its own crystalline form, as indeed may the eutectics in metal systems if they be obtained by appropriate heat treatment or by sufficiently slow

¹⁷ This glass is of the same composition as that employed by Holland and Turner, *J. Soc. Glass Tech.*, 1936, 20, 72, in their researches on the breaking strength of sheet glass under various conditions, and from which publication the above analysis is taken.

¹⁸ *J. Amer. Ceram. Soc.*, 1930, 13, 683.

¹⁹ For a description of the properties and crystal forms of the commonly occurring crystalline phases in commercial glass compositions, see Preston and Holland, *J. Soc. Glass Tech.*, 1937, 21, 395; 1938, 22, 82. This work with additions is to be published by the Council of the Society of Glass Technology in their Monograph series.

²⁰ See *The Properties of Silica*, by R. B. Sosman, *Amer. Chem. Soc., Monograph Series*. The Chemical Catalogue Co., New York, U.S.A., 1927.

cooling, and the eutectic is shown simply to be the simultaneous crystallisation of the two phases from a liquid saturated with respect to each of them.

The simultaneous nature of the separation is seen from the specimen shown in Fig. 5, in which both hexagonal tridymite and orthorhombic devitrite are crystallising side by side from the same crystal nucleus. Further examples of binary eutectic separation in fused silicates are given by Figs. 6 and 7. In these cases wollastonite,²¹ $\text{CaO} \cdot \text{SiO}_2$, was the primary phase, and the eutectic wollastonite-silica corresponding to separation along the binary eutectic line AF'C of Fig. 3. Again, each crystalline phase retains its characteristic crystal form, the silica in the form of small dendrites of cristobalite, the wollastonite in the form of long needles belonging to the monoclinic system.

Physical conditions have a marked effect on the form of crystallisation of silica as is shown by Figs. 8 and 9. At the glass-air interface tridymite tends to predominate, whilst in the body of the glass the silica phase is in general cristobalite.

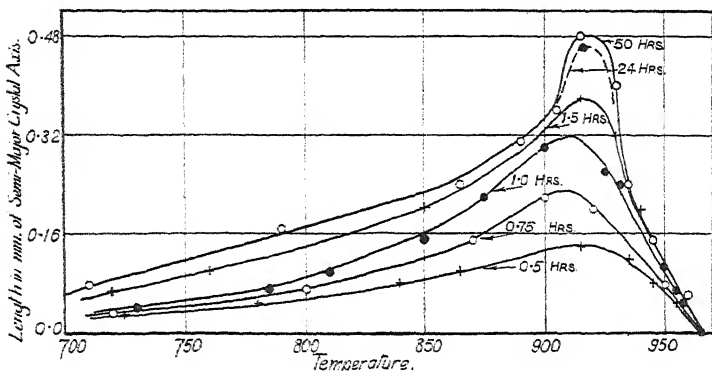


FIG. 3.—Crystal growth of devitrite ($\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$), the primary crystalline phase in a sheet glass composition at different temperatures determined by the gradient method after 0.5, 0.75, 1.0, 1.5, 24, and 50 hours' heating respectively.

Considerations of crystallisation processes have always assumed that crystal growth begins at a nucleus created, accidentally or artificially, by some discontinuity in the liquid phase, and in consequence proceeds the more rapidly at an interface. In actual fact crystallisation is often slower at an interface than in the body of the liquid, especially in glasses at the glass-air interface. The physical conditions at the interface determine the speed of crystallisation, and where the nuclei are not too close together the statement is generally true. This effect is demonstrated by the example of Fig. 10, which is a photograph of eutectic silica crystallisation at the glass-platinum interface. Of the eight cristobalite dendrites in the field of view, seven of them have their crystal centres on a metal grain boundary, *i.e.*, where there is also discontinuity in the metal and in consequence the glass-to-metal discontinuity is greatest at such positions.

²¹ See Holland and Preston, *loc. cit.*¹⁹, for a description of the occurrence of wollastonite as a devitrification product in glasses and its optical properties.

Crystallisation above T_M . The Effect of Saturation.

Between T_M and the liquidus temperature the experimental results show, Fig. 11, that the error will not be great, at least when compared with crystal growth measurements, if we conclude that crystal size or rate of growth is proportional to the interval below the liquidus temperature at which crystallisation takes place. The average liquidus surface is sufficiently flat, as indicated in Fig. 2, for this same relationship to be approximately true for the amount of primary crystalline

phase in equilibrium with the liquid phase at temperatures between the liquidus and binary eutectic temperatures. It seems reasonable to conclude that in this region the amount of crystalline material present after a given heat treatment is directly proportional to the amount of the particular crystalline phase which can be in equilibrium with the liquid phase at the temperatures of the measurements.

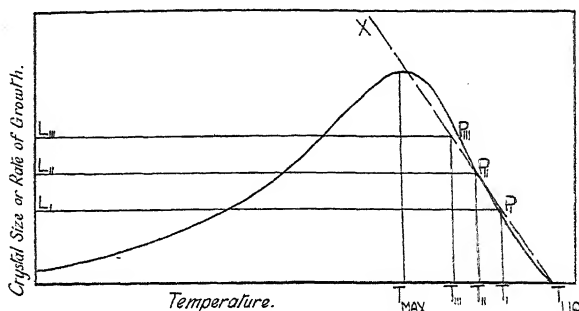


FIG. 11.—Idealised crystal growth-temperature curve.

phase which can be in equilibrium with the liquid phase at the temperatures of the measurements.

In this region between T_M and the liquidus crystallisation ceases much more quickly than below T_M , owing to equilibrium proportions of crystal and liquid phases having been attained. The interval ($T_{Liq.} - T$) may be regarded as the degree of supercooling²² and as some measure of the force causing crystallisation. Thus, to a first approximation in this region, we may say that

$$r \text{ (rate of crystal growth)} \propto (T_{Liq.} - T) \text{ (degree of supercooling).}$$

It is recognised that this statement is in fact an assumption which the experimental results substantiate because of the degree of error which must always exist in such crystal growth measurements.

Crystallisation below T_M . The Effects of Viscosity and Diffusion.

The combined effects of viscosity and diffusion in retarding crystal growth are illustrated by the microsections shown in Figs. 12 and 13 for the same material, namely, cristobalite. In the one case the cristobalite has separated out from a comparatively fluid open-hearth furnace slag,²³ and in the other from a much more viscous technical bottle-glass composition.¹⁹ The cooling processes in both cases may be considered comparable. There is a marked difference in size of the cristobalite dendrites in the two cases. Similarly, in Fig. 14 the skeleton crystals of cristobalite in the open-hearth slag are very much coarser

²² In a manner somewhat analogous to the analytical procedure of naming the factor ($Q - S$) the degree of supersaturation in which Q is the total amount of material momentarily formed in solution, and S the true solubility.

²³ Whiteley and Hallimond, *J. Iron Steel Inst.*, 1919, 99, 199.

than similar skeleton crystals, as exemplified by Fig. 15, found in commercial glass compositions. It may be noted that at 1400° a commercial soda-lime-silica glass has a viscosity of about 200 poises, *i.e.*, it is about as viscous as treacle at room temperatures.

Below T_M it has frequently been assumed that the greatly increased viscosity with falling temperature is responsible for the progressive diminution in crystal growth in spite of the fact that the degree of supercooling is continually increasing. Finally the viscosity of a material such as a glass becomes so great that crystallisation is entirely suppressed and is impossible to achieve in any realisable time, and a pseudo-stable state is reached. It is possible to show how far this view may be substantiated and to indicate the nature of the empirical relationship between viscosity and crystal growth.

If, as is done in Fig. 16, for the region below T_M we plot \log (rate of crystal growth) for the primary crystalline phase of the same sheet-glass composition for which results have been given in Fig. 1, between

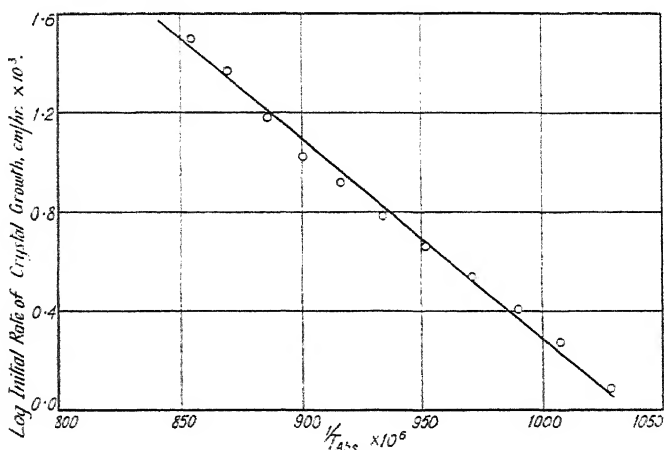


FIG. 16.—Relationship between rate of crystal growth and absolute temperature for devitrite at temperatures below that of maximum crystal growth.

the periods 0.0 and 0.5 hours against the inverse of the absolute temperature, we obtain a linear relationship. It is known that a similar relationship holds good between viscosity and absolute temperature²⁴ except that it is of opposite sign; we have,

$$\log \eta = \frac{A}{T_{Abs.}} + B,$$

$$\log r = \frac{-C}{T_{Abs.}} + D,$$

in which r = the rate of crystal growth in the temperature region below T_M , and A , B , C , and D are constants. Thus in this region it appears

²⁴ The equation $\eta = ce^{-A/T}$ is not an exact one, see Preston and Seddon, *J. Soc. Glass Tech.*, 1937, 21, 123, since the value of A is also a function of temperature. It is perhaps unfortunate that this viscosity equation is not always realised as being itself an empirical equation and is often accepted as being fundamental.

that we may employ, with some justification, as a first approximation the empirical relationship

$$r_{T_1}/r_{T_2} = \left(\frac{\eta_{T_1}}{\eta_{T_2}} \right)^{-C/A},$$

in which it is assumed that rate of crystal growth is universally proportional to some function of viscosity, the index $-C/A$ being entirely independent of the units in which the two properties are measured. In the particular case under examination the value of this index is $\frac{8200}{12000}$ or approximately two-thirds.

It may be noted that a similar relationship is known to be true over a wide range of temperature for the electrical resistivity and viscosity of a glass. It is of the type

$$\frac{r_1}{r_2} = \left(\frac{\eta_1}{\eta_2} \right)^\beta$$

in which r is the electrical resistivity and β is apparently an index dependent on the type and atomic complexity of the glass and in known cases varies between 2.0 and 6.2.²⁵

An Empirical Relationship between Crystal Growth and Temperature for Viscous Liquids.

If, in the search for a relationship between crystal growth and temperature which would satisfactorily represent the results, the two assumptions found experimentally to be justifiable for the temperature regions above and below T_M are combined, we obtain

$$r = Ke^{-C/T_{\text{Abs.}}}(T_{\text{Liq.}} - T).$$

In this equation C is the slope of the $\log r - 1/T_{\text{Abs.}}$ line, and for the present case has been determined experimentally as 8200 (see Fig. 16).

Plotting the function $e^{-8200/T_{\text{Abs.}}}(965 - T)$ against temperature it will be found that although a curve of the correct type is obtained, the maximum does not occur at the experimentally determined temperature, but at about 850° , and the relationship is not satisfactory.

Consideration of Fig. 2 indicates that the proportion of crystalline material present at each temperature should be considered rather than a single crystal dimension; since for the crystal to grow a volume of liquid must be displaced against the viscous forces opposing crystallisation. If V be the volume of crystalline material present, then

$$\log V = \log r^3 + c = \frac{3 \times 8270}{T_{\text{Abs.}}} + E,$$

and if we employ this slope in the empirical equation obtained above, we have

$$r = Ke^{-24800/T_{\text{Abs.}}}(T_{\text{Liq.}} - T),$$

²⁵ Vide Babcock, *J. Amer. Ceram. Soc.*, 1934, 17, 329; also Preston and Seddon, *loc. cit.*²⁴.

and the curve resulting by plotting the function $e^{-24800/T_{\text{Abs.}}}(965 - T)$ against temperature is shown at B, Fig. 17,²⁶ and it will be noted that the maximum in the curve now coincides with the experimentally determined value of T_M .

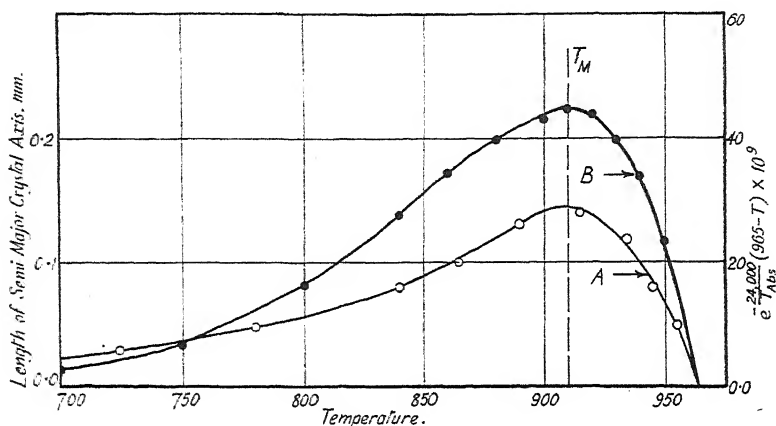


FIG. 17.—Curve A. Relation between crystal size and temperature for the initial heating period of 0.5 hrs. for crystallisation of devitrite from the sheet glass composition.

Curve B. Variation with temperature of the expression $e^{-\frac{24,000}{T_{\text{Abs.}}}}(965 - T)$.

Further, Fig. 18 shows that the relationship is fairly satisfactory over the temperature range 950° to 800° , the value of K in this range being approximately 0.31×10^7 if crystal growth be expressed in millimetres for the initial heating period of 0.5 hours, showing that crystal

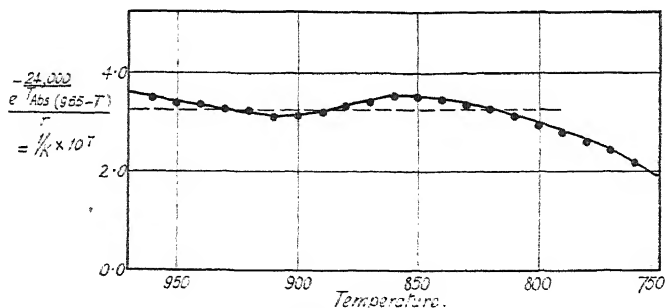


FIG. 18.—Variation of the ratio $e^{-\frac{24,000}{T_{\text{Abs.}}}}(965 - T)/r$, indicating the accuracy of the empirical relationship.

growth at temperature T is approximately proportional to the expression $e^{-24800/T_{\text{Abs.}}}(965 - T)$.

It will be noted from this Fig. that for approximately 60° on either side of the temperature of maximum crystal growth, the relationship holds

²⁶ In this curve a value of 24,000 has been used in the calculations instead of 24,800 for the reason stated later.

quite well, there being only a negligible variation in the value of K in this range when compared with the unavoidable errors of crystal growth determinations.²⁷ Below 800° possibly other factors come into play which have not been taken into account. For example, we have assumed that the degree of supercooling is proportional to the temperature interval below the liquidus, but we cannot expect such a simple relationship to hold over a wide range of temperature.

In the viscosity equation

$$\log \eta = A/T_{\text{Abs.}} + B,$$

the value of A for this glass is known to be of the order of 12,000; this is sufficiently close to $\frac{24800}{2}$ for us to write to a first approximation

$$\begin{aligned} r, \text{ the rate of crystal growth} &= K e^{-2A/T_{\text{Abs.}}(T_{\text{Liq.}} - T)} \\ &= K \left(\frac{1}{\eta} \right)^2 (T_{\text{Liq.}} - T). \end{aligned}$$

Now the reciprocal of viscosity is known as mobility, and thus we have for the complete curve that crystal growth is directly proportional to the square of the mobility and to the interval below the liquidus temperature at which crystallisation occurs. Mobility is a decreasing function with falling temperature, whilst the degree of supercooling increases.

A factor which has not yet been considered, and which must influence the rate of crystal growth, is the rate of diffusion of material necessary to form the solid crystalline phase. At first sight it would appear that in the above equation no account has been taken of the rate of diffusion of essential components through the liquid to form this crystalline phase. However, the empirical relationship obtained is of such a form that it apparently implicitly contains a term depending on diffusion. For lack of data we must assume that for a given constituent such diffusion is proportional to the mobility of the liquid in which it takes place, and then the term (mobility squared) in the equation appears to have some justification.

If, *a priori*, we assume that the rate of crystallisation is inversely proportional to the viscosity, directly proportional to the rate of diffusion of essential constituents, and directly proportional to the degree of supercooling, all of which appear to be reasonable assumptions, we obtain

$$\begin{aligned} r &= K_1 \left(\frac{1}{\text{viscosity}} \right) (\text{rate of diffusion}) (\text{degree of supercooling}) \\ &= K_2 \left(\frac{1}{\eta} \right)^2 (T_{\text{Liq.}} - T), \end{aligned}$$

which is the form of the equation found above to represent satisfactorily the experimental results. Although data is only presented in this paper for a particular glass composition, work on other glasses indicates that the equation is applicable, with a suitable constant, to crystal growth in a wide range of silicate glasses.

²⁷ See Preston, *J. Soc. Glass Tech.*, 1940, 24, 139, for a discussion of these errors.

It remains to point out that such curves as those shown in Fig. 1 and subsequent Figs. relate only to the primary crystalline phase. Below the temperature of the first appearance of binary eutectic a further curve will be required for the second crystalline phase. This curve will not normally show a maximum but will lie entirely in the region below T_M . Similarly, in a three-component system a third curve will be required below the ternary eutectic temperature for the complete representation of the crystallisation processes in such a system. Further, the equation obtained is only valid during the early period of crystallisation, that is, whilst the rate of crystallisation at a given temperature remains appreciably constant.

Summary.

Fused silicates such as technical glasses and slags because of their high viscosities are ideal materials for observations of crystallisation processes in supercooled solutions. Eutectic separation is clearly shown to be the simultaneous deposition of different crystalline phases from the liquid phase saturated with respect to each constituent, and each material preserves its own crystalline form in contrast to the more generally observed characteristic eutectic structures obtained by the rapid cooling of very much more fluid metallic alloys.

An empirical equation has been given relating rate of crystal growth to the temperature and viscosity of the supercooled liquid phase which has some theoretical significance and which may be applied to a wide range of silicate glasses. It is probable that such an equation may be of general application to the case of crystallisation of supercooled solutions.

The author desires to express his gratitude to Professor W. E. S. Turner, O.B.E., D.Sc., F.R.S., for his constant interest and encouragement, and for the facilities afforded in the Department of Glass Technology where the researches described above have been carried out.

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THE PROPERTIES OF DETERGENT SOLUTIONS. PART XI. ELECTROPHORETIC MOBILITIES IN DODECYL PYRIDINIUM IODIDE SOLUTIONS.

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BY J. POWNEY AND L. J. WOOD.

The remarkable influence of very small concentrations of dodecyl pyridinium chloride on the mobility of Nujol droplets in water has been described in a previous communication.¹ It was shown that where there is an electrostatic attraction between the suspended particles and the paraffin chain ions a high mobility can be obtained in solutions exhibiting little or no interfacial activity. Mobility data have now been obtained for different types of particles in solutions of the cation-active

¹ Powney and Wood, *Trans. Faraday Soc.*, 1940, **36**, 57.

salt, dodecyl pyridinium iodide, $C_{12}H_{25} \cdot C_5H_5N \cdot I$ (hereafter referred to as $C_{12}PyI$) and the effect of added electrolytes has also been investigated. The experimental technique was the same as that previously described.^{1, 2}

Results and Discussion.

Mobilities in Dodecyl Pyridinium Iodide Solutions.

The mobilities of Nujol in solutions of dodecyl pyridinium iodide at 25° and 60° C. are shown in Fig. 1. Data for ilmenite and glass particles at 25° are also included. The Nujol curve for 25° is very similar to that obtained with dodecyl pyridinium chloride, high positive mobilities

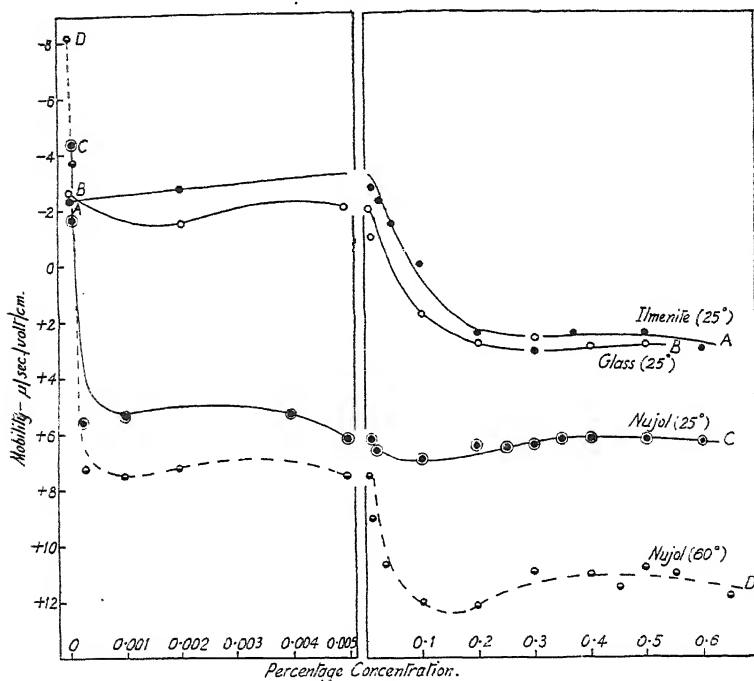


FIG. 1.—Mobilities of various particles in dodecyl pyridinium iodide solutions.

being reached at very low concentrations as before. The sensitivity is indicated by the fact that over the concentration range 0 to 0.0002 % the mobility changes from -4.3 to $+5.5 \mu/\text{sec.}/\text{volt}/\text{cm.}$

The mobility curve at 60° is of the same form as that at 25° and at the higher concentrations the change of mobility with temperature conforms approximately³ to the simple relationship $u_1\eta_1 = u_2\eta_2$ where u represents the mobility of the particle and η the viscosity of the dispersion medium. This relationship does not hold, however, at the very low concentrations of $C_{12}PyI$, where the observed mobilities at 60° C. are only about 75 % of the values calculated from the corresponding data at 25°. A similar behaviour was previously found in the case of sodium laurate solutions,² although in this instance the divergence occurred

² Powney and Wood, *Trans. Faraday Soc.*, 1940, **36**, 420.

³ Freundlich, *Colloid and Capillary Chemistry*, London, p. 248.

over the entire concentration range studied and was attributed to a decrease in the degree of adsorption of the surface-active ions with increasing temperature.

The distinct difference in behaviour of hydrophobic particles of Nujol and hydrophilic particles of ilmenite and glass in very dilute solutions of $C_{12}PyI$ is of particular interest. In both instances there is strong electrostatic attraction between the negative particles and the positive pyridinium ions, but under these conditions drop-number measurements indicate that there is no interfacial activity at the oil-solution interface. Under the same conditions, however, glass is rendered strongly hydrophobic, which suggests that in the latter instance there is at these low concentrations definite interfacial adsorption of the pyridinium ions presumably with the hydrophobic chain oriented towards the solution. This is confirmed by observations of contact angles on clean glass surfaces which show that the angle of contact *increases* with increasing concentration of $C_{12}PyI$ over the range 0.001 %, and subsequently decreases to zero at the higher concentrations at which a positive mobility is observed. The hydrophobic film formed at the very low concentrations is extremely resistant to rinsing, and even to prolonged boiling in pure water. In view of this, it is possible that the transition to a hydrophilic surface at higher concentrations is due to the adsorption of a second film giving rise to a bimolecular layer. An outward orientation of the hydrophobic chain may account for the fact that the mobility of the glass particles remains negative and essentially constant over this concentration range. Serious difficulties arise, however, in attempting to explain the high positive mobilities of oil drops

in very dilute solutions of $C_{12}PyI$ for no lowering of interfacial tension is apparent whilst the positive mobility would seem to indicate a fair degree of adsorption of the long chain cations at the oil-solution interface. Other anomalies of this type have been described by the present authors⁴ at the recent Faraday Society discussion on "The Oil-Water Interface." Any interpretation of this behaviour is at present difficult, since there are no means available for measuring *directly* the degree of adsorption at the oil-solution interface.

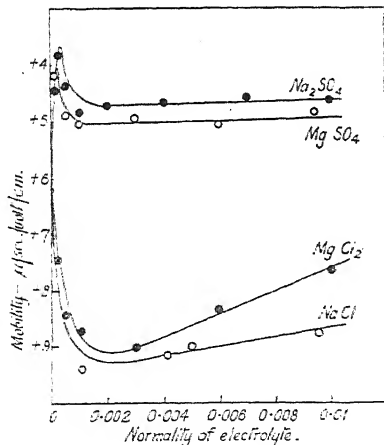


FIG. 2.—Mobilities of Nujol in 0.01 per cent dodecyl pyridinium iodide solutions containing added electrolytes.

Influence of Electrolytes.

The influence of added simple electrolytes on the mobility of Nujol in very dilute (0.01 %) and in relatively strong (0.5 %) solu-

tions of $C_{12}PyI$ has been studied. In the more dilute solutions interpretation of the changes of mobility is complicated by changes of surface conductance⁵ arising from the addition of electrolytes. It will be seen from Fig. 2 that at a concentration of 0.01 % the change of mobility

⁴ Powney and Wood, *Trans. Faraday Soc.*, 1941, 37, 156.

⁵ Bikerman, *ibid.*, 1940, 36, 154, 713.

produced by added electrolytes is dependent mainly upon the valency of the added anion. Although the sulphate ion produces an appreciable decrease in positive mobility whilst the chloride ion actually increases the mobility, it is possible that in both instances the zeta potential is decreased.

At the higher $C_{12}PyI$ concentration the mobility is most probably controlled by the formation of an adsorbed film of long chain ions, since there is now a very considerable lowering of interfacial tension.⁴ The sensitivity of this system to added anions is relatively low, presumably on account of the incidental presence of a fairly high concentration of iodide ions (Fig. 3).

The mobility of Nujol in $C_{12}PyI$ solutions containing a fixed amount of added NaCl has also been determined (Fig. 4). By comparison with the curve obtained in the absence of added electrolyte, it will be seen that the influence of the sodium chloride becomes very marked only when the concentration of $C_{12}PyI$ is below 0.03 %. It is of interest to note that there is no apparent interfacial activity in this region, and that at higher concentrations where the interfacial activity increases rapidly the influence of sodium chloride becomes negligible.

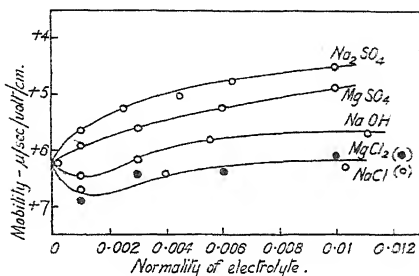


FIG. 3.—Mobilities of Nujol in 0.5 per cent. dodecyl pyridinium iodide solutions containing added electrolytes.

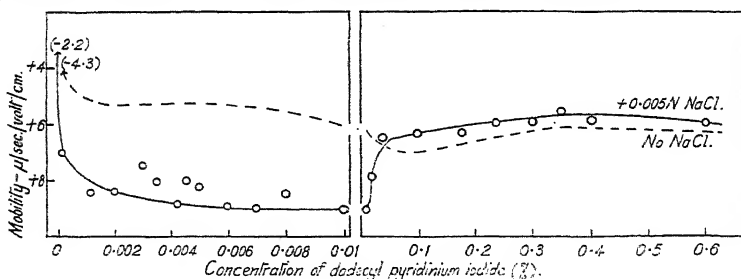


FIG. 4.—Effect of added NaCl on the mobility of Nujol in dodecyl pyridinium iodide solutions.

Summary.

Measurements of the electrophoretic mobility of dispersions of Nujol, ilmenite and glass in solutions of the cation-active salt, dodecyl pyridinium iodide are described. The effect of added electrolytes on the mobility has also been investigated. In very dilute solutions the behaviour of oil drops is markedly different from that of solid particles such as ilmenite and glass.

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STUDIES IN HYDROGEN OVERVOLTAGE AT HIGH CURRENT DENSITIES. PART II. THE INFLUENCE OF THE SOLVENT.

BY A. HICKLING AND F. W. SALT.

Received 24th January, 1941.

The hydration energy of the hydrogen ion is taken into account in those modern theories¹ of overvoltage which are founded upon quantum mechanical principles, although the implications of the inclusion of this factor are not, in general, stressed, and, in particular, the effect of using a medium in which the hydrogen ion is not appreciably solvated has not received attention. Moreover, the environment of the hydrogen ion has recently been made of central importance in an application of the theory of absolute reaction rates to overvoltage by Eyring, Glasstone and Laidler,² who regard the slow process, which is the fundamental cause of overvoltage, to be the transfer of a proton from a molecule of solvent in the solution to one on the electrode surface. It is apparent, therefore, that on any of these theories the hydrogen overvoltage in non-aqueous solutions might be expected to differ markedly from that observed when water is used as solvent, and in particular the authors of the absolute reaction rate theory predict that overvoltages in alcoholic media should be lower than in aqueous solutions, since the transfer of a proton from a molecule of alcohol attached to the solvent to one on the electrode will require a smaller energy of activation than the corresponding process involving water molecules where solvation is more pronounced.

Experimental work in non-aqueous solvents is complicated by the high resistance of the solutions, since very small polarising currents must be used in measurements of overvoltage by the direct method in order to avoid large resistance errors, and the use of these minute currents necessitates stringent precautions to eliminate depolarisers produced by oxidation of alcoholic solvents; furthermore, the choice of a satisfactory reference electrode is a problem of some difficulty. It will be seen from the following survey of the small amount of work which has been done, that in nearly all cases insufficient attention has been given to one or more of the above points, and consequently the results of these measurements are of doubtful reliability.

Carrara³ determined the minimum overvoltages of twelve metals in solutions of sulphuric acid or potassium hydroxide in water, and methyl and ethyl alcohols after an arbitrary time using a hydrogen reference electrode. With fewer than half the metals were the results in the alcoholic solvents appreciably different from those in water, and in these cases it is doubtful whether the amounts by which the overvoltages were diminished in the non-aqueous solutions can be considered significant in

¹ See, for example, Gurney, *Proc. Roy. Soc. A*, 1931, **134**, 137; Horiuti and Polanyi, *Acta Physicochim. U.R.S.S.*, 1935, **2**, 505.

² Eyring, Glasstone and Laidler, *Trans. Amer. Electrochem. Soc.*, 1939, **76**, Preprint 26, 331; *J. Chem. Physics*, 1939, **7**, 1053.

³ *Z. physikal. Chem.*, 1909, **69**, 75.

view of the admitted uncertainty as to the position of the break point in the current-potential curves. Swann and Edelmann⁴ studied hydrogen overvoltages for a number of metals in a solution of sulphuric acid in glacial acetic acid, using a chloranil reference electrode which had previously been indirectly calibrated against a hydrogen electrode in the same solution. They worked at fairly large currents and obtained extremely high values which rose rapidly as the current density was increased; it is apparent from their figures that the large resistance errors which must have been present completely mask any true over-voltage values. Lewina and Silberfarb⁵ investigated hydrogen over-voltage on mercury in ethyl alcohol solutions of hydrogen chloride with current densities of 10^{-6} to 10^{-2} amp./sq. cm.; a hydrogen reference electrode was apparently used but its constancy and reversibility are not discussed. They record results showing that Tafel's equation is obeyed up to a current of 10^{-3} amp./sq. cm. when deviations set in; their over-voltage values were slightly less than in aqueous solution. Some additional values for mercury in non-aqueous solvents have been obtained by Novoselski,⁶ who compared the overvoltages in sulphuric acid solutions in water, methyl alcohol, ethyl alcohol, and ether at low current densities; slight lowerings of overvoltage were noted in the alcoholic solvents. Measurements of hydrogen overvoltage in liquid ammonia at -50° C. have recently been carried out by Pleskov⁷; the values were higher than in aqueous solution, but in view of the very different conditions it is doubtful to what extent comparison is justifiable.

It is apparent that the data listed above do not enable any general conclusion to be drawn as to the influence of solvent upon hydrogen overvoltage, and a comprehensive investigation has therefore been carried out over the current density range 10^{-3} to 1 amp./sq. cm. for representative metals by the technique developed in Part I of this series,⁸ which eliminates resistance error. Ethylene glycol has been used as the main solvent, and the results have been checked by further observations in ethyl alcohol and cyclohexanol.

Experimental.

Choice of Solvent.—In choosing a solvent suitable for work on over-voltage at high C.D.'s in non-aqueous solutions, the following points must be borne in mind: (a) availability, (b) ease of drying, (c) susceptibility to reduction by nascent hydrogen, (d) stability and conducting power of the solutions. For the present work it was desired to use hydrogen chloride as electrolyte, so as to obtain results directly comparable with those in aqueous solution (Part I⁸), and therefore the conducting power of saturated solutions of this substance in some thirty-seven solvents (roughly dried), including alcohols, esters, hydrocarbons, phenols, ethers, and organic and inorganic chlorides, was investigated in a semi-quantitative manner. It was found that only the solutions in the alcohols, acetone, ethyl acetoacetate and formic acid had the requisite low resistance, and the last three substances failed to satisfy one or more of the other criteria listed above; hence the present study has been limited to alcoholic solvents. Of these

⁴ *Trans. Amer. Electrochem. Soc.*, 1930, 58, 75.

⁵ *Acta Physicochim. U.R.S.S.*, 1936, 4, 275.

⁶ *J. Phys. Chem. U.R.S.S.*, 1938, 11, 369; *Ber. Inst. physik. Chem. Akad. Wiss. Ukr. S.S.R.*, 1938, 11, 125. Reported in *Chemical Abstracts*, 1939, 4136; 1940, 2262. These papers are not readily accessible in the original, and it is thus impossible to judge the reliability of the experimental methods used.

⁷ *Acta Physicochim. U.R.S.S.*, 1939, 11, 305.

⁸ Hickling and Salt, *Trans. Faraday Soc.*, 1940, 36, 1226.

ethylene glycol appeared to be most suitable, since it is readily obtained substantially water-free by distillation alone, and gives excellently conducting solutions of high stability (*vide infra*). As a check upon the results obtained in glycol, ethyl alcohol and cyclohexanol were used as additional alcoholic solvents of different types.

Purification of Solvents and Preparation of Solutions.—Commercial "pure" ethylene glycol was distilled at ordinary pressure, and the fraction boiling at 197–198° (corr.) was collected and used. In view of its markedly hygroscopic nature, the storing of the glycol and the preparation of solutions in it of hydrogen chloride of known strength were carried out in an atmosphere of dry hydrogen in the enclosed apparatus shown in Fig. 1. Immediately after purification, the glycol was transferred without exposing it to air to the 3 l. storage flask A, the air in the apparatus being swept out with hydrogen. When a solution was required for use, about 70 c.c. of the glycol were forced through the taps T_1 and T_2 into the saturation vessel B by hydrogen pressure, and by reversing T_1 the inlet

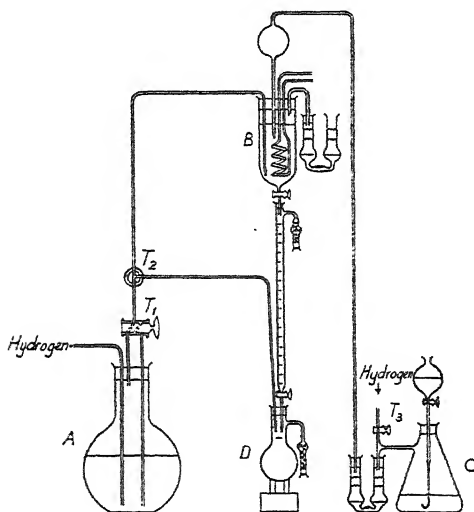


FIG. 1.—Preparation of hydrogen chloride solutions in glycol.

tube was cleared of liquid and a stream of hydrogen passed through the glycol in B. Dry hydrogen chloride, generated by running hydrochloric acid into concentrated sulphuric acid in C, was then passed into B, the solution being cooled by circulating ice water through the cooling coil. Solution of the gas took place rapidly, aided by the stirring of the glycol produced by the passage of the hydrogen, and when saturation was approached the hydrogen chloride stream was stopped and the delivery tube cleared by leading in hydrogen via tap T_3 . The burette was washed through with several small portions of the solution, and then 10 c.c. were run out for titration with

NaOH. After the strength of the solution had been ascertained (usually about 6 N), a volume was run from the burette into flask D, such that on making up to the mark with glycol, driven over from the storage vessel via T_2 , an exactly N-HCl solution in glycol was obtained.

The stability of the glycol solutions was investigated and found to be remarkably good. Thus the titre of a 5 N-solution with respect to NaOH was found to be unchanged 50 hours after preparation of the solution, and even in the course of a week the change in strength was less than 3 %. As a further check, the conductivity (which, as shown below, gives a very sensitive indication of the presence of water) of a N-solution of HCl in glycol at 25° was measured over a period of 3 days; no change could be detected. Nevertheless, to obviate any possibility of reaction between the HCl and glycol, which would lead, of course, to the formation of water, fresh solutions were prepared daily.

Ordinary absolute ethyl alcohol was dehydrated by refluxing with ethyl succinate and metallic sodium, followed by distillation, according to the method of E. L. Smith⁹ which is said to give a product containing

⁹ J. Chem. Soc., 1927, 1288.

less than 0.01 % water. Cyclohexanol was purified by fractional distillation at ordinary pressure using a short column and collecting the fraction boiling at 160-160.5° (corr.). This product melted at 20.8°, and by further distillation *in vacuo*, a fraction boiling at 67-68° at 8 mm. was obtained of m.p. 21.2°. No further elevation of the m.p. could be effected, and although this value is low compared with that of Lange¹⁰ (25.46°), it is in good agreement with the value of 20.6° quoted by Sidgwick and Sutton¹¹ for carefully purified cyclohexanol. Solutions of HCl in ethyl alcohol and cyclohexanol were prepared in small quantities as required; esterification in the first solvent is known to be very slow,¹² and direct experiment showed it to be inappreciable in cyclohexanol over the period of overvoltage observations.

Reference Electrode.—The constancy and reversibility of the hydrogen electrode in glycol solutions of HCl was investigated by setting up concentration cells with two hydrogen electrodes at atmospheric pressure. Platinum wires coated with platinum black and carefully dried were employed. It was found that these cells attained constant and reproducible e.m.f.'s in about 30 minutes after starting the hydrogen stream; they maintained these values when the passage of gas was stopped, and returned to them rapidly after polarisation. It thus appears that the hydrogen electrode in glycol possesses a high degree of reversibility, and is a suitable reference electrode in overvoltage measurements. As an additional precaution against any shift in the potential of the reference electrode during the overvoltage experiments with glycol and the other solvents, two independent hydrogen electrodes enclosed in the same sheath were used, and these were continually checked against each other. Furthermore, to ensure that the electrodes were in equilibrium with the solutions, they were cathodically polarised for a short time at the beginning of each set of experiments, and then given at least 30 minutes in the hydrogen stream to reach a steady state before any observations were made.

Estimation of Water in the Glycol Solutions.—As it is practically impossible in work in non-aqueous solvents completely to exclude all traces of water, it was considered desirable to have some method whereby the amount of water present could be continually checked. It appeared likely that measurement of the electrical conductivity of the solutions would afford such a method, and so the conductivity of a N-solution of HCl at 25° in glycol containing various amounts of water was determined. The somewhat surprising result was obtained that small additions of water, up to about 4 % by volume, markedly *decreased* the conductivity; further amounts of water then increased the conductivity rapidly as expected. Similar observations for other alcohols have been made by Goldschmidt.¹³ The relevant data obtained are given in Fig. 2, A and B. The conductivity measurements were made at 25° in an enclosed cell with platinised platinum electrodes; a period of about 30 minutes was required after filling the cell for the conductivity to reach a steady value, and the results were then found to be satisfactorily reproducible. The value for N-HCl in glycol containing no water was obtained with a specimen of glycol which had been repeatedly distilled until no further lowering of resistance could be attained; for the solutions containing water, known amounts of aqueous N-HCl were added to this solution. It will be noted that the variation of conductivity with water content is accurately linear up to at least 1 % water, and that it forms a

¹⁰ *Z. physikal. Chem. A*, 1932, 161, 77.

¹¹ *J. Chem. Soc.*, 1930, 1324.

¹² Kailan, *Monatsh.*, 1907, 28, 559; Harned and Fleysher, *J. Amer. Chem. Soc.*, 1925, 47, 82.

¹³ *Z. physikal. Chem.*, 1914, 89, 129; *Z. Elektrochem.*, 1914, 20, 473; also Goldschmidt and Mathiesen, *Z. physikal. Chem.*, 1926, 121, 153.

very sensitive means of estimating small amounts of water present, 0.02 % by volume being readily detectable. Graphs similar to that in Fig. 2B were obtained for several concentrations of HCl, approximately N, so that by interpolation the water content of any of the solutions likely to be encountered in the electrolytic work could be ascertained. In every case the amount of water in the cell solution was determined both before and after each set of overvoltage experiments, the concentration of HCl being first checked by titration. The water content of the glycol solutions after use was found in no case to exceed 0.5 %, and the average for all the experiments recorded in this paper was 0.36 %.

General Conditions.—The electrolytic cell was essentially similar to that previously used,⁸ but had the double hydrogen electrode mentioned above and was protected from moisture by H₂SO₄ bubblers in the outlet tubes; the anode compartment, containing the filter paper plug, was kept in a desiccator between experiments. Cylinder hydrogen, after the oxygen had been removed by alkaline pyrogallol solution, was dried by passage through CaCl₂, concentrated H₂SO₄, and P₂O₅ consecutively; it was then bubbled through a sample of the electrolyte and finally into the cell.

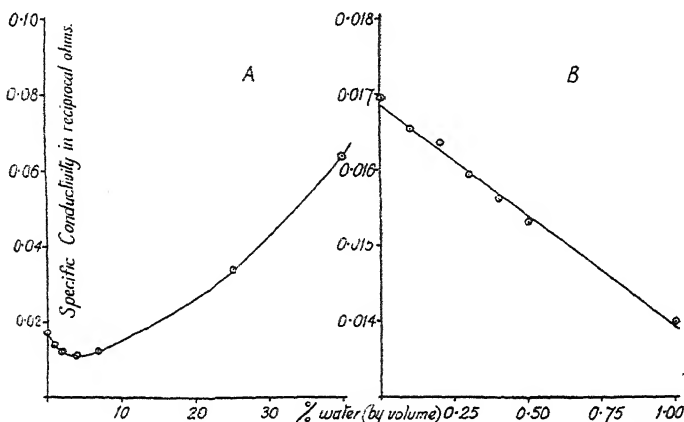


FIG. 2.—Conductivity of N-hydrogen chloride in glycol-water mixtures.

Overvoltage measurements were made according to the methods described in Part I⁸ in N-HCl solutions over the C.D. range 10^{-3} to 1 amp./sq. cm., using wire electrodes of 0.1 sq. cm. area. In certain cases reproducible values could not be obtained at the highest C.D., where energy dissipation is considerable, and with the cyclohexanol solutions, which were relatively poor conductors, observations had to be confined to the range 10^{-3} to 10^{-2} amp./sq. cm. The temperature was maintained as far as possible at $16 \pm 1^\circ$, but at the highest current sometimes rose to 20° .

Results.

Mercury, tungsten, and platinised platinum were chosen as the chief electrodes for study, since previous experience⁸ had shown that reproducible overvoltage results were most easily obtained with these materials, and furthermore they cover the whole range of high, medium, and low overvoltages; additional observations in glycol only were made with a tin and an electrodeposited lead electrode since these are representative examples of the metals which, in aqueous solution, show marked departure from Tafel's equation, $\eta = a + b \log I$ (η —overvoltage, I —current density, a and b —constants). The overvoltage results are summarised in Table I,

those previously obtained in aqueous solution being inserted for comparison, and the experimental values of b (obtained from the initial slopes of the $\eta - \log I$ graphs) are also included. In Fig. 3 the $\eta - \log I$ graphs

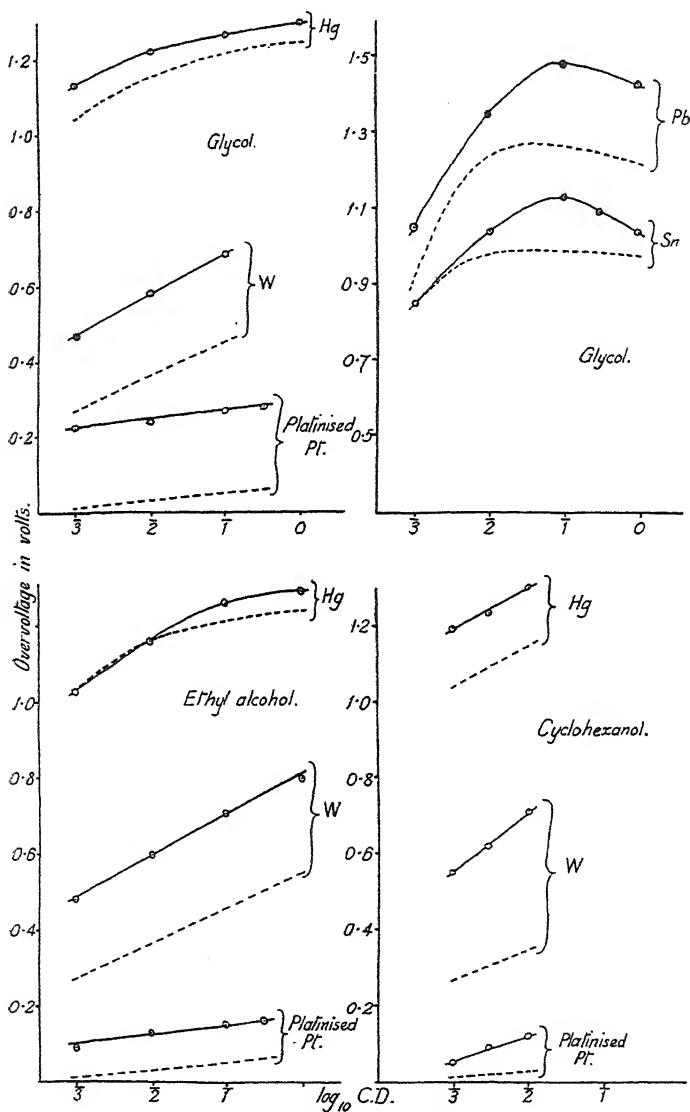


FIG. 3.—Overvoltage— \log C.D. graphs.

are given, additional overvoltage measurements at intermediate C.D.'s having been made where necessary to define the curves; the broken lines represent the behaviour previously observed under identically similar conditions in aqueous solution.

Discussion.

The results listed in Table I and the graphs in Fig. 3 lead to a number of conclusions which may be briefly summarised:—

(a) In no case is the hydrogen overvoltage less in the alcoholic solvents than in water.

TABLE I.

Material.	Solvent.	Overvoltage (volts).				b.
		C.D. 10^{-3} Amp./sq. cm.	10^{-2}	10^{-1}	1	
Hg	Water	1.04	1.15	1.21	1.24	0.12
	Glycol	1.13	1.22	1.26	1.29	0.10
	Ethyl alcohol	1.03	1.16	1.26	1.29	0.13
	Cyclohexanol	1.19	1.30	—	—	0.10
W	Water	0.27	0.35	0.47	0.54	0.09
	Glycol	0.47	0.58	0.68	—	0.11
	Ethyl alcohol	0.48	0.60	0.71	0.80	0.12
	Cyclohexanol	0.55	0.71	—	—	0.16
Platinised Pt.	Water	0.01	0.03	0.05	0.07	0.02
	Glycol	0.23	0.24	0.27	—	0.02
	Ethyl alcohol	0.09	0.13	0.15	—	0.04
	Cyclohexanol	0.05	0.12	—	—	0.07
Pb	Water	0.91	1.24	1.26	1.22	>0.3
	Glycol	1.05	1.35	1.48	1.43	0.3
Sn	Water	0.85	0.98	0.99	0.98	0.2
	Glycol	0.85	1.04	1.13	1.04	0.2

(b) In general, the shape, slope, and relative positions of the $\eta - \log I$ graphs are not substantially different from those observed in aqueous solution.

(c) Where any shift of overvoltage does occur, it is in an upward direction in the alcoholic solvents, but the differences are small except in special cases. Thus the

average differences for the various electrodes in passing from water to the other solvents are as shown in table opposite.

The conductivity measurements which have been made seem to indicate unmistakably that the state of solvation of the hydro-

gen ion in glycol is widely different from that in water; they are most readily interpreted on the view that solvation in glycol is not very strong, and that the subsequent hydration of the hydrogen ion on the addition of water leads to a diminution in its velocity with a consequent initial decrease in conductivity.¹⁴ Goldschmidt¹³ arrived at a similar view

¹⁴ It might be suggested that the initial decrease of conductivity is due to the presence of a maximum in the viscosity—composition curve for glycol—water mixtures. Measurements of the viscosity, however, showed no such maximum, and there was a continuous decrease in the viscosity on the addition of water. (Cf. also Dunstan, *J. Chem. Soc.*, 1905, 87, 11.)

	Glycol.	Ethyl Alcohol.	Cyclohexanol.
Hg	+ 0.07	+ 0.03	+ 0.15 volt
W	+ 0.21	+ 0.24	+ 0.32
Platinised Pt	+ 0.22	+ 0.09	+ 0.06
Pb	+ 0.17	—	—
Sn	+ 0.07	—	—

from a study of other alcohols, including ethyl alcohol.¹⁵ Since, therefore, it has been shown that overvoltages in the alcoholic solvents are not markedly different from those in aqueous solution, it is difficult to resist the conclusion that the environment of the hydrogen ion is *not* a primary factor in conditioning hydrogen overvoltage. The results lend no support to the absolute reaction rate theory of Eyring, Glasstone and Laidler,² which predicts that the overvoltage should be lower in alcoholic solvents, and are not in accord with those theories based on quantum mechanics in which the hydration of the hydrogen ion is an essential postulate.

It would not be expected on any view of hydrogen overvoltage that results in non-aqueous solutions should, in general, be *identical* with those in water, since a number of secondary factors may play a part. Thus the solvents may exert specific poisoning actions on the electrodes, and as has been shown experimentally,¹⁶ this usually results in a rise of overvoltage and an increase in *b*, particularly with the catalytically active, low overvoltage metals. Furthermore, the physical properties of the electrolyte, in particular surface tension, are known to have some influence on overvoltage,¹⁷ and these are generally very different in the non-aqueous solutions from those in water.

Summary.

1. Hydrogen overvoltage measurements have been made in the current density range 10^{-3} to 1 amp./sq. cm. for mercury, tungsten, platinised platinum, tin, and lead electrodes in N-HCl solutions in ethylene glycol; supplementary observations have been carried out in ethyl alcohol and cyclohexanol.

2. In no case is the hydrogen overvoltage less in the alcoholic solvents than in water, and in general the shapes, slopes, and positions of the overvoltage — log C.D. graphs are not substantially different from those in aqueous solution.

3. It is concluded that the environment of the hydrogen ion is not a primary factor conditioning hydrogen overvoltage, although the nature of the solvent may cause minor variations due to secondary influences.

The authors gratefully acknowledge a grant from the British Association for the Advancement of Science (to F. W. S.).

¹⁵ See also Millet, *Trans. Faraday Soc.*, 1927, **23**, 515.

¹⁶ See, for example, von Náray-Szabó, *Naturwiss.*, 1937, **25**, 12; Bowden, *Proc. Roy. Soc. A*, 1929, **126**, 107.

¹⁷ Cf. Möller, *Z. physikal. Chem.*, 1908, **65**, 226; *Ann. Physik*, 1908, **25**, 725; Thiel and Breuning, *Z. anorg. Chem.*, 1913, **83**, 329; MacInnes and Adler, *J. Amer. Chem. Soc.*, 1919, **41**, 194; Glasstone, *Trans. Faraday Soc.*, 1925, **21**, 36; Onoda, *Z. anorg. Chem.*, 1927, **165**, 193.

THE MECHANISM OF THE BREAKDOWN OF ORGANIC PROTECTIVE FILMS IN WATER.

BY J. T. KENDALL AND L. MASSEY.

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The mechanism by which organic protective films in water breakdown is necessarily complex because of the number of factors involved. These factors are not fully understood, and empirical methods are therefore employed in producing water-resistant organic films. The present paper attempts a more fundamental formulation of such factors, and investigates them experimentally.

Using various varnishes and pigments, films were made and the following properties studied:—water solubility, water permeability, water

THE INFLUENCE OF THE PIGMENTS ON THE PAINT-FILM PROPERTIES.



absorption, pH value and hydrolysis. These properties were chosen as being probably the most important primary factors involved in breakdown, for water must first come into intimate contact with the film (hence the importance of solubility, permeability and absorption), and chemical reaction can then take place (hence the importance of pH value and hydrolysis).

The varnishes and pigments studied were:—

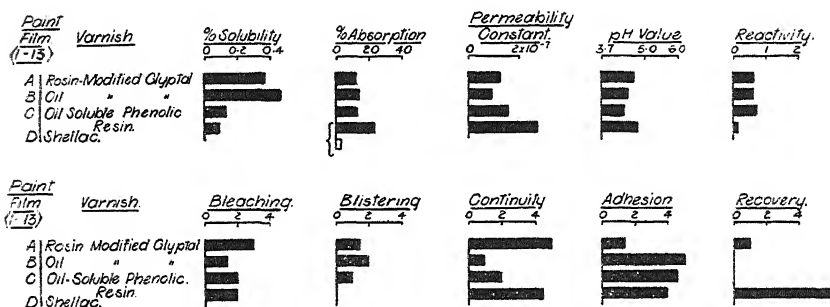
Varnishes—(A) Rosin-modified glyptal varnish. (B) Oil-modified glyptal varnish. (C) Oil-soluble phenolic varnish. (D) Shellac.

Pigments—1. (No pigment.) 2. Carbon Black. 3. Lithopone. 4. Monastral blue and lithopone. 5. Permanent red and lithopone. 6. Titanium dioxide. 7. Zinc oxide. 8. Antimony oxide. 9. Barytes. 10. Prussian blue. 11. Ultramarine. 12. Yellow iron oxide. 13. Zinc chrome.

Using combinations of one pigment with one varnish, fifty-two different films were thus obtained. In the experimental data represented diagram-

THE INFLUENCE OF THE VARNISHES ON THE PAINT-FILM PROPERTIES.

FIG. 2



matically, Fig. 1 shows averaged data for varnishes A-D, thus indicating the influence of the pigment on the properties of the films; and Fig. 2 shows averaged data for pigments 1-13, thus indicating the influence of the varnish.

It was found impossible to use the same amount of pigment for all films. The pigmentation is given in Table I.

The paints were prepared by grinding in the pigment with a palette knife on a glass plate. Films were prepared on amalgamated tinned iron plates, and were dried in air at room temperature for one week, immediately prior to test.

TABLE I.—PIGMENTATION.

Films.	
50 % Varnish base	A, B — 3, 6, 7, 8, 9, 11, 12, 13. and C.
50 % Pigment	
50 % Varnish base	A, B and C — 4, 5.
5 % Pigment	
45 % Lithopone	C.
70 % Varnish base	A, B and C — 2, 10.
30 % Pigment	
70 % Varnish base	D — 2, 3, 6, 7, 8, 9, 10, 11, 12, 13.
3 % Pigment	
27 % Lithopone	D — 4, 5.
100 % Varnish base	A ₁ , B ₁ , C ₁ , D ₁ .

(Varnish base = non-volatile content of varnish.)

Water Solubility.

The percentage of water-soluble material in the pigment was found by extracting the pigment with boiling water and determining the solid content of the cooled filtrate. By this method the small quantities of water-soluble impurities are completely dissolved, while a solution of the pigment, saturated at room temperature, is obtained. The water solubility, as measured, is the sum of these two. In general, the solubility due to the sparingly soluble salt which is the chief component of the pigment can be neglected in comparison with the solubility of the impurities.

This is not, of course, true for such comparatively soluble pigments as zinc chrome.

A direct measurement of the water-soluble material in the varnish by evaporating down an aqueous extract is impossible, since much of the water-soluble material will consist of volatile and easily decomposed organic compounds. An indication of the amount of water-soluble material present can, however, be obtained from conductivity measurements on an aqueous extract. Difficulty in obtaining an aqueous extract (owing to the stability of the varnish/water emulsion) was overcome by adding carbon tetrachloride to the varnish. From the measured conductivity a value for the molecular concentration was obtained, using the known straight-line relationship for a strong electrolyte. The solutions used were so dilute that this approximation is sufficiently accurate. Assuming, arbitrarily, a mean molecular weight of the water-soluble material of 100, the concentration of the extract in g. per cc. was calculated. The value of 100 was chosen as most probable, having regard to the nature of the water-soluble substances, glycerine, phthalic acid, etc.

From the measured percentages of water-soluble material in pigments and varnishes, the percentages in the paint films can be calculated by simple addition. The results are shown in Figs. 1 and 2. This calculation is not strictly justified, for chemical reaction between pigment and varnish may produce compounds of different solubility from those originally present.

Water Permeability.

The permeation of water through a film can be represented by the equation,

$$W = \frac{D \cdot A \cdot t \cdot (p_1 - p_2)}{x},$$

where W = weight of water passed through film; x = thickness; A = area; t = time; p_1 and p_2 = vapour pressures on each side of film; and D = "permeability constant."

This expression is derived from Fick's law and holds strictly for films where diffusion only takes place (*e.g.*, paraffin wax, or polystyrene films). For the organic films considered here it is approximately true where sorption of the vapour by the film has reached equilibrium. The validity of the equation has been investigated by Taylor, Herrman and Kemp¹ while a picture of the diffusion process in terms of Fick's law has been drawn by R. M. Barrer.^{2, 3, 4}

The experimental method used, was to seal the free film over the open end of a wax cup containing water, place the cup in a desiccator and weigh it at intervals. By this arrangement one side of the film is exposed to air saturated with water vapour, while the vapour pressure on the other side is substantially zero. No exceptional precautions were taken to keep the wax cup at constant temperature, and the saturation vapour pressure of water was taken as 15 mm. of mercury.

Since for the films used it was to be expected that sorption would take place to a considerable extent, it was necessary to find out how long the sorption conditions took to reach equilibrium. This was done by plotting the permeability constant of the film against time. When Fick's law is obeyed, under equilibrium conditions, the constant should not vary. The graph of D plotted against t is shown in Fig. 3, for representative

¹ *Ind. Eng. Chem.*, 1936, 28, 1255.

² *Trans. Faraday Soc.*, 1939, 35, 628.

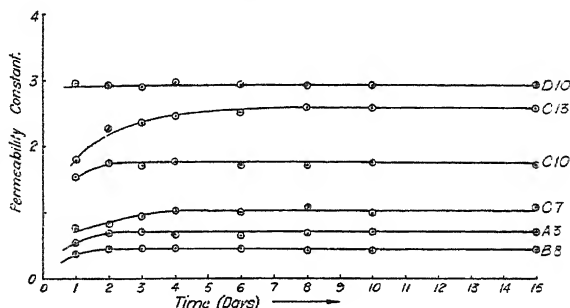
³ *Ibid.*, 644.

⁴ *Ibid.*, 1940, 36, 644.

films. It is seen that films prepared from varnish D (shellac) reach equilibrium in less than 24 hours; while for films prepared from the other varnishes equilibrium is in general reached in 24-48 hours; exceptions being films pigmented with zinc oxide and zinc chrome, for which substantial equilibrium is only reached after 6-8 days. (The anomalous behaviour of these two pigments will be discussed in the section dealing with pH value and reactivity.)

VARIATION OF PERMEABILITY CONSTANT WITH TIME
OF PERMEATION.

FIG. 3.



Even under equilibrium conditions Fick's law is only an approximation when sorption takes place. It was therefore thought necessary to investigate how the permeability constant varied with thickness. A number of representative films were tested, and the results showed that within the limits of accuracy of these measurements the permeability constant is independent of thickness. The dependence of the permeability constant on temperature and on relative vapour pressure on the two sides of the film was not investigated. These factors were approximately constant throughout the series of measurements.

For the films studied the permeability constants are shown in Figs. 1 and 2. These represent the number of grams of water which would pass through a centimetre cube of the material in one hour under unit vapour pressure gradient. The correspondence of diagrams for absorption and permeability is very clear indeed. It is apparent that a large sorption of water is associated with a high permeability. A rough correspondence between solubility and permeability can also be noted. This can be understood, since the presence of water-soluble material may increase the "wettability" of micro-pores (assuming sorption takes place by capillarity) if the material is hydrophilic. The resulting increase of sorption leads to an increase in permeability. Fig. 1 shows that the permeabilities of films 6 (titanium dioxide) and 9 (barium sulphate) are abnormally high when considered in relation to solubility. This is explainable by their extremely high reactivities, leading to strong adsorption of water and hence higher permeability.

The mechanism of permeation of water can now be pictured. For metals the centre to centre atomic distances are smaller than the diameter of a water molecule, and permeation cannot take place. For paraffin wax the atomic distances are about four times the diameter of a water molecule, and permeation by diffusion is possible.

For varnish films of a polar nature adsorption and ionization of water molecules can take place, and their effective diameter thus be much reduced. Furthermore, an adsorbed ion has great mobility parallel to the surface (as strikingly demonstrated by Volmer and Estermann in their experiments on the growth of crystals). An adsorbed vapour molecule is thus in a far better position to permeate through the film

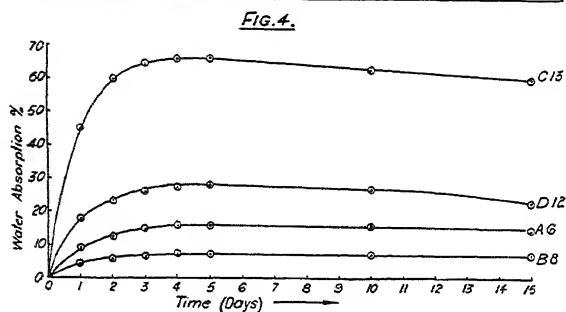
than an unadsorbed molecule. In addition, sorption of vapour molecules swells the varnish film and increases the dimensions of the micro-porous structure. Much more rapid diffusion is then possible.

The influence of pigments on water permeability is seen to be the result of changes effected in (i) the magnitude of adsorption forces, (ii) the dimensions of the micro-porous structure, (iii) the shape of the vapour pressure gradient through the film, and possibly other factors. Measurements of permeability—after a constant rate of flow has been reached—do not tell much about the relative importance of those factors. It would be most instructive to carry out accurate measurements of permeability before equilibrium conditions had been reached. An investigation in this direction has been made by Payne and Gardner.⁵

Water Absorption.

When a film is placed in water, soluble material is dissolved out and water is absorbed. The present experiments neglect the former effect, which is seldom important. The water absorption was measured by placing a weighed piece of the dry film in water and reweighing it

VARIATION OF WATER ABSORPTION WITH TIME OF ABSORPTION.



after leaving for one week at room temperature. The results are shown in Figs. 1 and 2, where the water absorption is expressed as the number of grams which would be absorbed by 100g. of the dry film.

The effect of temperature on water absorption was not investigated. The time taken to reach equilibrium was determined, since values for water absorption can only be compared for films in equilibrium. Measurements on representative films, given graphically in Fig. 4, showed that absorption was complete after 5 days. The slight decrease after this time was due to continued leaching out of water-soluble material.

Varnish films exposed to water vapour also absorb moisture. Films were exposed on one side to air saturated at 15–20° C., and on the other to dry air. The film thickness before and after permeation was measured. The difference represented the volume of water absorbed, and was expressed as volume of water per 100 cc. of dry film. The results obtained by the two methods were found to be closely parallel, except for varnish D (shellac). The significance of the divergence in this case is not apparent, and it can only be said that under the conditions of test used, the absorption of water vapour by shellac is abnormally small. This absorption is shown unshaded in Fig. 2 for shellac.

A varnish film may be considered as a colloidal gel system, consisting of a multitude of fine capillaries. If the water "wets" the material composing the walls of the capillaries then the van der Waals and chemical forces operating, will cause the water to penetrate into the

⁵ *Ind. Eng. Chem.*, 1937, 29, 893.

varnish film and result in considerable swelling. The greater the molecular forces, and the larger the area of the capillary walls along which they can act, the greater will be the swelling pressure, and the larger the water absorption. This simple state of affairs is complicated by the presence of water-soluble substances in the film. These can have a profound influence on the water absorption by—

(1) Mechanically increasing the size of the capillaries, so that macro-pores tend to be formed.

(2) Altering the magnitude of the van der Waals and chemical forces.

(3) Where the pigment is water soluble the film may act as a semi-permeable membrane, and the film will swell by osmosis.

From the general correspondence of absorption with water solubility it may be inferred in the case of the more soluble pigments that osmosis plays an important part. In the cases of titanium dioxide and barium sulphate the reactivity of these substances may be important in increasing the van der Waals and chemical forces. With a pigment such as carbon black, it is possible that the decrease of absorption, compared with the unpigmented varnish film, is due to increase in size of capillaries and decrease of capillary activity.

In an attempt to derive further information as to how absorption depends on solubility, a more simple system was studied. Measurements of water absorption were made on films prepared from two specimens of varnish B (glyptal base), one of which had been washed as free as possible from water-soluble material. In order to avoid a stable varnish/water emulsion the varnish was thinned with carbon tetrachloride before washing and filtering. The results of duplicate measurements are shown in Table II, from which the effect is seen to be small.

TABLE II.—EFFECT OF WATER SOLUBILITY ON WATER ABSORPTION.

Varnish.	% of Water-soluble Material in Varnish Base.	Water Absorption (% by Weight).
B (1) Unwashed	0.60	4.78
B (2) Washed	0.10	4.51

TABLE III.—ELECTRICAL BREAKDOWN VALUES AFTER IMMERSION IN WATER.

Conditioning.	Electrical B.D.V.	(kV per 0.001 inch.)
(After 1 hour in Oven at 100° C.)	(1) Washed Film. (0.10% Soluble.)	(2) Unwashed Film. (0.60% Soluble.)
No further treatment .	8.4	8.4
10 seconds in water .	—	8.3
1 hour in water .	5.2	3.3
24 hours in water .	2.9	3.2
1 hour in 5 % NaCl .	5.3	4.2
24 hours in 5 % NaCl.	3.4	3.2

by reducing both the number of ions and the water absorption.

The results are shown in Table III, from which it can be seen that

available, it was thought worth while to make a very brief investigation into how far the presence of water-soluble materials in a varnish film affected its electrical breakdown value after immersion in water. The removal of these materials should favour increased breakdown voltage

the reduction of water-soluble material has had no discernible effect on electrical breakdown value after 24 hours' immersion. After 1 hour's immersion there is a noticeable difference, so it may be that solubility does affect the time taken for electrical B.D.V. to fall. The addition of 5 % of sodium chloride to the water has apparently little effect. These results seem to show that attempts to improve electrical breakdown value after water immersion, by reducing water-soluble material to an extremely small amount, are not likely to have much success. A final decision on this point must, however, await a more complete investigation.

It is known that the water absorption of a varnish film can be decreased by adding salts to the water.⁶ It was found experimentally that by increasing the salt concentration sufficiently, absorption of water by the film could be almost completely stopped; and, considered purely from an osmotic point of view, an apparently isotonic concentration could be measured. This can be explained in alternative ways:—

(1) If osmosis is the major factor, absorption of water is complete when there is set up a dynamic equilibrium of osmotic pressures. The film may be considered as a semi-permeable membrane.

(2) If capillarity is the chief factor, the film may be considered as a large number of capillaries into which water molecules can penetrate. Salt molecules can block these capillaries and thus reduce water absorption.

In practice one may be sure that both these factors (and possibly others) will operate in varying degrees. Further investigation is desirable.

pH Value and Reactivity.

In this investigation pH values of pigments, varnish films and paint films were measured by extracting 1 g. with 50 ml. of neutral distilled water at 95-100° C. for one hour, and measuring the pH of the aqueous extract by means of a glass electrode system. Negligible hydrolysis takes place under these conditions, practically identical results being obtained by extracting with water at 15-20° C. for 24 hours, except in the case of shellac films. The pH value measured in this way represents the free available acid present in the pigment or film. The pH values experimentally obtained are shown in Figs. 1 and 2.

From the measured pH values of pigments and varnish films calculated values for the paint films can be obtained, simply by taking the arithmetic mean of the two values. The justification for this simple approximate calculation is given in the following short discussion of the relationship between the pH value of a solution and the relative concentrations of various acids and alkalis present. In Fig. 5 are shown neutralization curves obtained by means of a hydrogen electrode system. The effect of the different dissociation constants is clearly seen. In the case of the addition of a pigment to a varnish the acid will be provided by the varnish, and will necessarily be a weak organic acid (e.g., phthalic acid). The base will be provided by the pigment. With these reactants a curve similar to (2) or (4) will be followed, depending on the strength of the base. So long as the final pH of the mixture is less than 7 both types of curve can be approximately represented by a straight line. This is in actual fact the case.

The calculated and experimental pH values of the paint films differ considerably. These divergencies may be due to the following factors:—

⁶ J. Alexander, *Colloid Chemistry, Principles and Applications*, Chapman and Hall, 1939.

(1) The method of calculation takes an incomplete account of the dissociation constants of the different substances. It assumes that the dissociation constants of the acids are small.

(2) Hydrolysis constants are ignored. The degree of hydrolysis involved during the aqueous extraction essential to the method of pH determination may not be the same for all the substances.

(3) No account is taken of the adsorption of ions in a colloidal system.

(4) Chemical reaction between varnish and pigment is not taken into account.

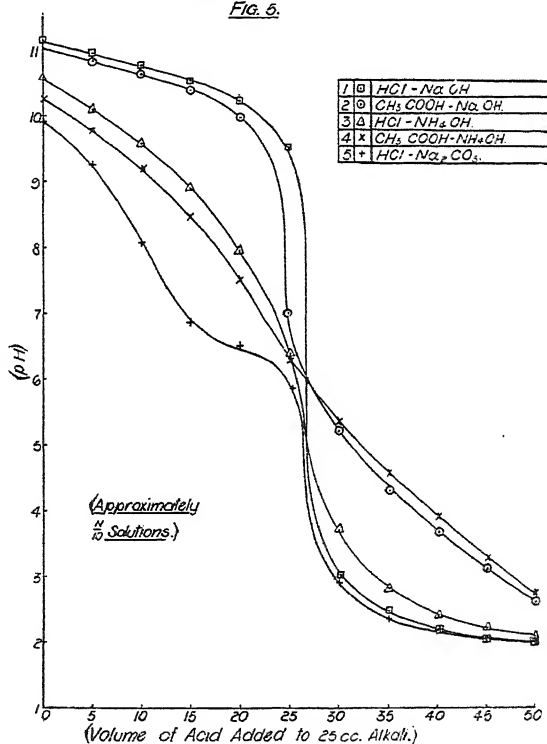
Owing to the impossibility of obtaining information as to how far the first two factors are operative, it is assumed that their effect is small compared with the combined effect of factors (3) and (4). This seems a probable hypothesis. The difference between calculated and experimental pH values of the paint films is therefore taken to be a measure of the amount of physical and chemical reaction which has taken place between the pigment and the varnish base, and is termed the "reactivity" of the paint film. Values of the reactivity (calculated pH minus experimental pH) are shown in Figs. 1 and 2.

Comparing the diagrams of pH and reactivity with those showing absorption and permeability, it can be seen that large values of reactivity are associated with those films which have in relation to solubility a high absorption and permeability. Conversely, where low values of reactivity are obtained, low values of absorption and permeability result (e.g., antimony oxide and zinc oxide).

A negative reactivity, where the experimental pH is greater than the calculated pH , indicates that the result of chemical action between pigment and varnish base is to reduce the amount of available free acid. This would occur, in the case of an amphoteric compound such as zinc oxide, if the acidic-basic equilibrium tended to be in favour of the basic product. In this connection it is significant to note that zinc and antimony pigments have low reactivities, while titanium and barium

RELATIONSHIP OF pH TO ACID-ALKALI RATIO FOR VARIOUS ACIDS AND ALKALIS.

FIG. 5.



have exceptionally high reactivities. From this it could be predicted with a fair degree of certainty that, for example, calcium pigments would have a high reactivity, and tin pigments would have a low or even negative reactivity.

The pH values measured above were taken immediately after the films had dried for 7 days in air at 15-20° C. It was thought advisable to test any possible change in reactivity with time. Films of varnish B (glyptal base) pigmented with (1) titanium dioxide and (2) zinc chrome were tested. The results are tabulated and show how reactivity varies with time when the film is kept (a) in a dry atmosphere, (b) in a moist atmosphere.

TABLE IV.—CHANGE OF REACTIVITY WITH TIME.

Varnish B.	Reactivity.	
	Titanium Dioxide.	Zinc Chrome.
1. Original reactivity	2.04	—0.73
2. After conditioning in damp atmosphere for one week	2.09	—0.44
3. After conditioning in damp atmosphere for two weeks	2.05	—0.20
4. After conditioning in dry atmosphere for two weeks	2.05	—0.69
5. After conditioning in damp atmosphere for one week, and then in dry atmosphere for one week	2.10	—0.58

These results show that the reactivity of zinc chrome changes when the film is kept in a moist atmosphere. The effect would appear to be reversible, but this is not certain. In a dry atmosphere the reactivity of the zinc chrome films does not appear to change. For the titanium dioxide films reactivity remains substantially constant even in a moist atmosphere.

Owing to the small field covered, and the incompleteness of some of the measurements, the results given here only indicate the possibilities of the application of pH measurements for studying the chemical changes taking place in paint films. The interpretation of the concept introduced as *reactivity* is not in any way intended as final. Rather is it hoped that the lack of a precise interpretation may stimulate further work in this subject—which we believe offers a fruitful field of investigation.

Hydrolysis of Varnish Films.

When a varnish film is exposed to steam, chemical reaction takes place between the steam and the constituents of the varnish, as a result of which the condensate from the steam becomes progressively more acid. This factor of steam hydrolysis is very important in assessing the value of a varnish for use where it is exposed to steam.

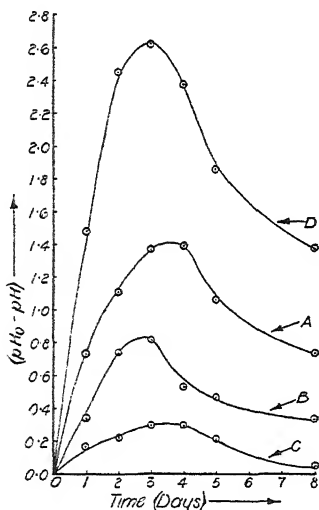
Unpigmented varnish films were drawn on tissue paper. After drying in air at room temperature for one week, a weighed quantity of the film was wrapped loosely around a glass rod, which was placed in the neck of a flask. A known volume of freshly distilled water was placed in the flask so that the water was not in contact with the film. The water was

allowed to boil under a reflux condenser for 24 hours, thus immersing the film in wet steam for that period. The water was then cooled, and its pH measured. A fresh lot of water was placed in the flask, and the procedure repeated. A series of pH values was thus obtained. Let pH_0 be the pH value of the varnish film as obtained by standing in water at 15–20° C. for 24 hours (*i.e.*, where negligible hydrolysis has taken place). Then the series of values ($pH_0 - pH_1$), ($pH_0 - pH_2$), ($pH_0 - pH_3$), etc., represents the extent to which hydrolysis of the film has taken place during each day. This series is shown graphically in Fig. 6. It can be seen from this graph that there is a striking difference in the stability to steam of the four varnishes.

During 24 hours' immersion in water at 15–20° C. it was assumed above that negligible hydrolysis takes place. The low pH value of the aqueous extract is due solely to solution of the acid constituents of the varnish. Successive extractions will therefore progressively remove the available free acid. This effect, which might be called water extraction rather than

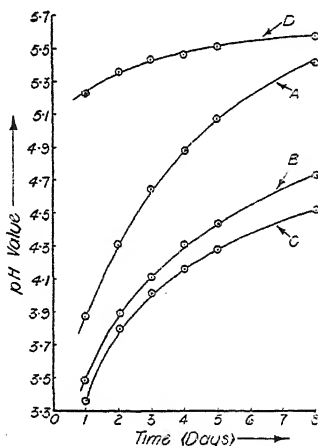
STEAM HYDROLYSIS.

FIG. 6.



WATER (20°C) EXTRACTION.

FIG. 7.



water hydrolysis, was investigated. Films were prepared as described above for steam hydrolysis. A weighed quantity was placed in a known volume of water (in the proportion of 1 g. of film to 50 ml. of water) at 15–20° C. for 24 hours, and the pH of the water measured. Fresh water was added, and the procedure repeated. The results are shown graphically in Fig. 7.

Breakdown of Films in Water.

The experimental procedure was as follows. The films were prepared on glass plates, dried in air at room temperature for one week, and immersed in distilled water at 15–20° C. At the end of two weeks the degree of breakdown was noted by assessing the following effects: (1) bleaching, (2) blistering, (3) film continuity, (4) film adhesion, and (5) recovery of continuity and adhesion on drying.

Bleaching was assessed by comparing the part of the film which had been immersed in the water with that part which had been above the

surface. Blistering was assessed by the number and size of the blisters formed. Continuity and adhesion were tested by scratching with a knife; if the film broke into pieces continuity was considered poor; if the film came away easily from the glass plate adhesion was considered poor. On drying the continuity and adhesion were generally almost completely

TABLE V.

Grade.	Bleaching and Blistering.	Continuity and Adhesion.	Recovery.
0	None	Excellent	Good
1	Very slight	Very good	—
2	Slight	Good	—
3	Definite	Fair	Fair
4	Very definite	Poor	—
5	Bad	Very poor	—
6	Very bad	None	None

recovered. This did not, however, hold for shellac films, where the recovery is really negative, for the film cracks off as it dries. This indicates the interesting result, that for *continuous* immersion in cold water shellac is a good film, while for *interrupted* immersion

it is much inferior to the other varnishes. The effects described above were graded according to the scale shown in Table V.

The dependence of breakdown on the following properties can be noted from the diagrams:—

(1) *Water Solubility*.—It can be seen that there is a general correspondence between breakdown and solubility. This is more apparent for blistering and bleaching of the films, but it is discernible for the other breakdown tests also. The solubility of films 1-9 is small and shows little variation, and through this series of films the influence of solubility on breakdown is undetectable. A second series of films 10-13 has a higher solubility, and in general shows higher breakdown values. Film 13 (zinc chrome) has an enormously higher solubility than the other films, but its breakdown values are not generally higher than for the other films of the series 10-13. Films made from varnishes C and D have a lower solubility than the corresponding films made from A and B. This difference seems to influence breakdown values for bleaching and blistering, but for continuity, adhesion and recovery of the films, other factors must have more importance.

From the preceding paragraph it can be seen that water solubility is an important factor influencing the breakdown of a paint film in water. Greater solubility tends to produce greater breakdown.

(2) *Permeability and Absorption*.—In as much as there is a general correspondence between these two properties and solubility, so there is a general correspondence between them and breakdown. Greater permeability and absorption tends to produce greater breakdown. Individual variations are difficult to follow, but there is a correspondence between breakdown and the abnormally high permeability and absorption of films 6 and 9, and the abnormally low permeability and absorption of film 7.

(3) *Steam Hydrolysis and Water Extraction*.—An examination of the curves for these properties shows a clear order of stability to water of C—B—A—D (the last named being the least stable). This is a specific property of the varnish, unrelated to any other physical property such as solubility. It is difficult to trace any connection between steam hydrolysis and breakdown in water at 20° C. but if breakdown tests

were carried out at higher temperatures no doubt a correspondence would emerge.

(4) *Chemical Constitution*.—The influence of the chemical nature of the varnish is very apparent. Thus, to take an example at random, varnish A has good adhesion, but poor continuity, while the reverse is true for varnish B. It was hoped to connect facts like this with differences in solubility, absorption, permeability, etc., but there is no apparent connection.

The chemical nature of the pigment exerts a more predictable effect. The *pH* value and reactivity, taken together, is an approximate definition of the chemical nature of the pigment. A correspondence between this and breakdown is apparent. A low reactivity (films 7 and 8) is associated with a high stability, a high reactivity (films 6 and 9) is associated with a low stability to water.

There is an unexpected correspondence between the electrode potential of the cation of the pigments with the breakdown tests. The pigment cations are shown in the Table below.

TABLE VI.

Pigment.	Chief Substances Present.	Cations.	
1			
2	Carbon		
3	Barium sulphate, Zinc sulphide	Ba ^{..} ,	Zn ^{..}
4	" " " "	Ba ^{..} ,	Zn ^{..}
5	" " " "	Ba ^{..} ,	Zn ^{..}
6	Titanium dioxide	Ti ^{....}	
7	Zinc oxide	Zn ^{..}	
8	Antimony oxide	Sb ^{...}	
9	Barium sulphate	Ba ^{..}	
10	Ferric ferrocyanide	Fe ^{...}	
11	Clay	Al ^{...}	
12	Ferric oxide	Fe ^{...}	
13	Zinc chromate	Zn ^{..}	

Considering the breakdown results, an approximate order of merit for the cations is



The correspondence of this with the electromotive series although not perfect seems almost too good to be due to coincidence. The oxides of the metals on the left of the series are commonly called *acidic*, of those on the right *basic*. This difference in chemical nature probably plays an important part in determining the stability of the varnish films towards water. An interesting continuation would be to investigate the breakdown of films containing other cations and examine more closely any dependence on the electromotive series.

Summary.

From the correlation of data given in the preceding section it is apparent that for maximum water stability of a film the following properties of the component varnish and pigments are desirable:—

(a) The varnish should have a small water-hydrolysis; and low solubility, permeability and absorption.

(b) The pigments should have low solubility, and when mixed with the varnish should give a low reactivity.

These may be taken as the broad fundamental principles on which the formulation of water-resistant films should be based. Much detailed investigation and correlation remains to be done, and it is hoped that this paper may have stimulated interest in such fundamental data.

The authors' thanks are due to Dr. A. P. M. Fleming, C.B.E., M.Sc., Director of Metropolitan-Vickers Electrical Company Ltd., and to the Company for permission to publish this paper.

*Research Department,
Metropolitan-Vickers Electrical Company Limited,
Manchester.*

NOTE.*†

Dr. J. P. Flory has been so kind as to draw our attention to the fact that his formula¹ mentioned in our paper published in these Transactions² has been derived to determine the size distribution in condensation polymers and was not primarily concerned with size distributions in degradation products. For the calculation of the size distribution in condensation polymers his formula, of course, holds without any assumptions and approximations.

We would also like to mention that recently a paper of Durfee and Kertesz was published³ which leads to essentially the same results as our own, although the methods applied are somewhat different.

* By H. Mark and R. Simha. *Cf. Degradation of Long-chain Molecules. Vol. 36*, p. 611.

† Received 16th July, 1940.

¹ See J. P. Flory, *J.A.C.S.*, 1936, **58**, 1877.

² H. Mark and R. Simha, *Trans. Faraday Soc.*, 1940, **36**, 611.

³ W. H. Durfee and E. T. Kertesz, *J.A.C.S.*, 1940, **62**, 1196. *Cf.* also J. P. Flory, *ibid.*, p. 1561.

REVIEWS OF BOOKS.

Analytical Processes. A Physico-chemical Interpretation. Second Edition by T. B. SMITH, PH.D., A.R.C.S., B.Sc. (London: Edward Arnold & Co., 1940. Pp. viii + 470. 18s.)

In preparing the second edition of this work the author has discarded a certain amount of matter from the old edition which is readily available in standard text-books of physical chemistry. At the same time the text has been enlarged by some 100 pages by the inclusion of much new material. The arrangement of the contents has undergone little change; indeed, the chapter headings of the first edition have been retained. There has, however, been a very thorough and effective revision of the text. Recent developments have been incorporated and working details are now given for a representative selection of quantitative exercises. Sets of questions are also included at the ends of chapters.

This is clearly a book which should be available to University students, for it deals fully with the underlying problems of analysis which so often present difficulty. The first part of the book is, in fact, a review of the physico-chemical basis of a wide range of familiar analytical processes such, for example, as the typical precipitations of barium sulphate, lead sulphate, ferric hydroxide and silver halides, various standard types of titration, oxidation-reduction titrations and electroanalysis. In many places, too, the author gives useful hints on manipulation. The second part of the book appears under the self-explanatory title "A critical examination of some of the theories employed"; and includes a discussion of supersaturation and crystallisation, of colloidal phenomena, and of complex ions. These chapters are full of interest, and one feels that they would provide an excellent tonic for those who regard analysis as a mere tool in chemistry. Equally this collection of information, much of which is not readily available elsewhere, should be of assistance to teachers in colleges and schools.

H. J. E.

Lunge and Keane's Technical Methods of Chemical Analysis.

Second Edition, edited by CHARLES A. KEANE and P. C. L. THORNE.
Volume IV. (London: Gurney & Jackson, 1940. Pp. xv + 963.
Price £4 4s.)

This volume virtually comprises seven text-books of varying importance, each dealing with the testing and analytical methods used in a special branch of chemical technology and written by one or more experts. They deal with (1) Coal Tar and Tar Products (370 pp.), (2) Textiles and Textile Chemistry (281 pp.), (3) Explosives (93 pp.), (4) Coal Gas Manufacture (66 pp.), (5) Matches and Fire Works (66 pp.), (6) Ammonia and Ammoniacal Liquors (20 pp.), and (7) Calcium Carbide and Acetylene (32 pp.). The inclusion of these seven branches in one volume, large though it be, makes the selection and treatment of material an exceedingly difficult problem. The authors of the section on Coal Tar and Tar Products seem to have been the most successful in these tasks and they have produced a valuable treatise. This almost stands by itself as an independent work, even though it is stated that "the original publications must be consulted when a determination purporting to be carried out by the standard methods is in hand". It is probably a hopeless task to deal satisfactorily with the large and ever expanding field of textiles and textile chemistry in 281 pages of bold print; this will account for the omissions and the somewhat general treatment. Hence the section has less value than the above-mentioned as an independent working guide and frequent use of other text-books and original papers will be inevitable. Much of the value of the section will be found in the exceedingly useful hints and ideas that it contains. The examination of textiles after finishing, chiefly by physical methods, is dealt with in an interesting and novel manner—after enumerating the properties of a textile which affect its behaviour in use, there follow descriptions of the principal methods whereby the properties are modified and of the defects which may arise from such operations and then methods are suggested by which the modifications are assessed. A sign of the times is the discussion of the newer detergents and wetting-out

agents. The section on Matches and Fire Works seems the least satisfactory. Anyone not an expert in this field will find little real guidance to the present situation as regards composition of products and modes of testing; the information on glue is somewhat inaccurate. In the section on Explosives there are too many references to sources of information not easily accessible. Calcium Carbide and Acetylene are dealt with in a business-like manner. The section on Coal Gas makes frequent references to Volume I.

Each of the fields of chemical industry dealt with needs a modern discussion of its appropriate analytical methods and the publishers are to be congratulated on bringing out this well-produced and exceedingly valuable work in these times.

C. H. S.

The Separation of Gases. By M. RUHEMANN. (The International Series of Monographs on Physics. Oxford, at the Clarendon Press. Dec. 1940. Pp. xiii + 283, with 148 Figures. Price 21s. net.)

During the past forty years large and flourishing industries have been developed in order to separate air into its constituent gases by methods involving the fractionation of liquid air. Similar low temperature methods are now being applied on the industrial scale to separate the constituents of other industrial gases, such as coke oven gas. The development of these industries forms an excellent example of the application of the principles and data of physical science to large scale problems, and Dr. Ruhemann is to be congratulated on writing a book which shows this application so clearly. It should be read not only by chemists, physicists and engineers interested in low temperature work with gases, but also by advanced students and others who are interested in the application of "academic" science to industrial problems.

The author starts with a brief description of the properties and uses of the common gases of industrial importance which form the raw materials of the gas separation industries. Then, assuming a sound working knowledge of the phase rule and of thermodynamics, he gives good summaries of the phase rule of binary and ternary liquid-vapour systems, and of the thermodynamics of systems in two-phase equilibrium. These summaries are followed by descriptions of the apparatus used by experimenters to obtain data of the liquid-vapour relationships of gas mixtures, and a survey of the results so far obtained. The theoretical principles and uses underlying the chief components of a low temperature gas separation plant are then briefly outlined. A chapter follows on heat, work and entropy in which it is shown how total heat and entropy diagrams for gas mixtures can be built up from the data available. As the process of the separation of gases by fractionation requires the production and maintenance of low temperatures, refrigeration plays an important part in such a process, and a chapter is therefore devoted to the principles underlying the liquefaction of gases. As air is the gas for which the methods of low temperature fractionation have been most completely worked out, the separation of air is described in four chapters. In the first, air is treated as a binary mixture and the development of the Linde double air column from the single Linde column is shown. In the second

the principles underlying the various commercial separation plants are described and compared. The third chapter is devoted to the effect and efficiency of plate columns and shows how these may be calculated. The results from this chapter are applied in the fourth to the problem of the separation of the rarer components of air and of the effect of these rarer gases on the working of oxygen and nitrogen separation plants.

The final chapters of the book give a brief survey of the industrial developments and of the possibilities of the separation of coke oven gas, methane and helium from natural gas, and of olefines from cracker gas.

The book is very well illustrated with good diagrams, although one, Fig. 16, is on rather too small a scale to be readily intelligible. The addition of an isometric drawing of the p - t - x surfaces of the liquid-vapour region of a binary mixture would have helped in following the section on the phase rule in Chapter II.

As has been stated, the author assumes a sound knowledge of the phase rule and of thermodynamics and it is a pity that he does not give a reference to such a book as Rivett's "The Phase Rule," as he does to Guggenheim's "Modern Thermodynamics." Also on page 198 he gives a relation, deduced from the kinetic theory of gases, for which a reference to a suitable text-book would have been helpful.

R. O. G.

An Introduction to the Kinetic Theory of Gases. By SIR JAMES JEANS. (London: Cambridge University Press, 1940.) Pp. 311. Price 15s. net.

In any book from the pen of Sir James Jeans we expect to find elegance, clarity and originality. In this new work we are not disappointed.

It is essentially an abridged version of the well-known *Dynamical Theory of Gases*, but mathematically it is much less formidable. It should, indeed, be quite within the powers of competent students of chemistry and of experimental physics. The experimental background of the theory receives much more attention in this new version than in the original, which is a great advantage. Another interesting characteristic of the book is the introduction of lucid but quite elementary preliminary treatments of some matters usually considered rather abstruse, for example, the neat introduction to the equipartition principle by direct calculation of the energy exchanges on impact.

The chemist will, perhaps, regret that partition functions and their uses are not dealt with, but there is so much that is illuminating in the book that to criticise it for what it does not contain would be ungracious.

C. N. H.

Physical Science in Art and Industry. By DR. E. G. RICHARDSON. (London: The English Universities Press, Ltd., 1940. Pp. xi + 293. Price 15s. net.)

The story of the applications of physical science to various problems of art and of industry is a fascinating one, and few are better qualified to tell the story than is Dr. Richardson. He has an eye for the essentials, and can simplify, without over-simplifying, the problem in hand; he

writes lightly, and knows the spirit of the phrase, *vulgariser sans abaisser*—the motto adopted by the publishers of the famous Armand-Colin series of scientific books. His present book is more technical in outlook than his *Physical Science in Modern Life*, but it is nonetheless pleasant reading, and may be read with profit alike by the educated layman and by the professional physicist who, cultivating one corner of the garden intensively, is at times more ignorant than the layman of what is going on in another corner.

The topics discussed are varied and well-chosen: the physics of locomotion; applications of physics to the pottery and the textile industries, to the culinary art, to building materials and to architectural problems; physics on the farm and down the mine; science and the musician; physics and the art of war. These are the principal subjects on which the author dilates agreeably and accurately.

The book is well produced and deserves success.

A. F.

Electron-inertia Effects. By F. B. LLEWELLYN. (Cambridge University Press, 1941. Pp. x + 104. Price 7s. 6d. net.)

Electron-inertia effects are no new story. As the author remarks, "such matters as the anomalous dispersion of light, the dependence of the dielectric constant of certain media upon the frequency of the applied voltage, and various aspects of spectroscopy come within this classification."

But in these systems, the inertia effects concerned are not the result of forces deliberately applied to the electrons *ab extra*, and it is with this latter class—the phenomena, *e.g.* exhibited in vacuum tubes when the movements of electrons are determined by controlled external forces—that the book is concerned.

The author develops the fundamental equations for the systems under review, using practical units "rather than an agglomeration of electrostatic and electromagnetic units all stirred together in one and the same equation, and seasoned with a pepper of 4π ." He discusses in consecutive chapters direct current relations, the first-order solution, first-order relations in diodes and in negative-grid triodes and second-order effects. The concluding chapter deals briefly, *inter alia*, with the high-frequency magnetron and Barkhausen-Kurz oscillations.

The book is a most useful addition to the series in which it appears.

A. F.

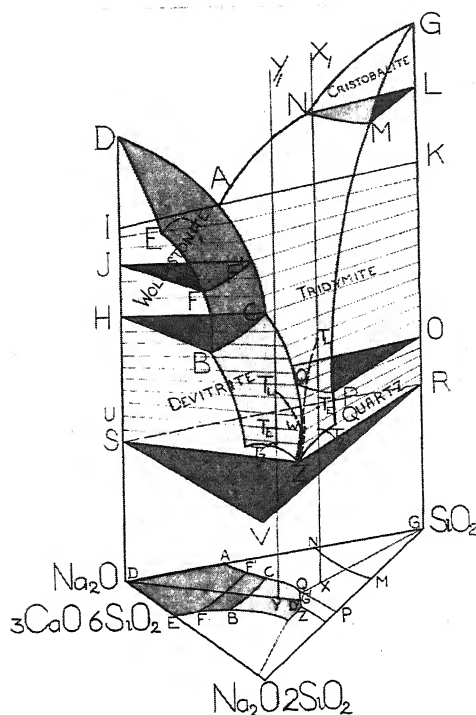


FIG. 2.—Perspective view of the equilibrium model of the soda-lime-silica system of importance in the study of commercial glass compositions.*

- ANGMPZQCF'A, is the liquidus surface of mixtures having silica as the primary crystalline phase,
 DAF'CBFED, is the liquidus surface of mixtures having wollastonite, $\text{CaO} \cdot \text{SiO}_2$, as the primary crystalline phase,
 BCZB, is the liquidus surface of mixtures having devitrite, $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$, as the primary crystalline phase,
 AF'CZ, is the binary eutectic line,
 IACZS and KACZR, are the binary eutectic surfaces,
 Z, is the ternary eutectic formed between devitrite, silica, and sodium disilicate,
 SVR, is the ternary eutectic plane,
 LMN and OPQ, are transition planes representing the cristobalite-tridymite and tridymite-quartz boundaries,
 JFF', is the transition plane marking the boundary between the high and low temperature forms of wollastonite, and
 HBC, is the peritectic plane at which temperature devitrite is formed by a peritectic reaction between wollastonite and the liquid phase.

* In this diagram the sodium disilicate corner has been cut away to expose the binary eutectic valley between silica and wollastonite or devitrite.

[See page 213.]

PLATE III.



FIG. 4.—Devitrite ($\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$)-silica binary eutectic separation in a sheet-glass composition after heating for 20 hours at 775° . The lath-like devitrite crystals, visible in the top left-hand corner, are some 8 to 10 times greater in length than the christobalite dendrites. $\times 550$.

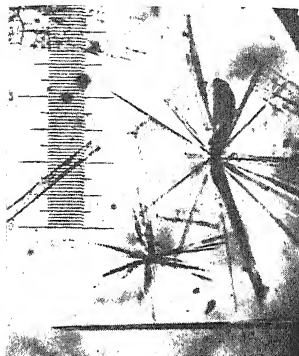


FIG. 5.—Example of tridymite-devitrite eutectic. Hexagonal tridymite crystal is growing from same crystal nucleus as the devitrite spherulite. $\times 50$.



FIG. 6.—Wollastonite ($\text{CaO} \cdot \text{SiO}_2$)-cristobalite eutectic formed on surface of bottle-glass composition at about 1100° . $\times 100$.

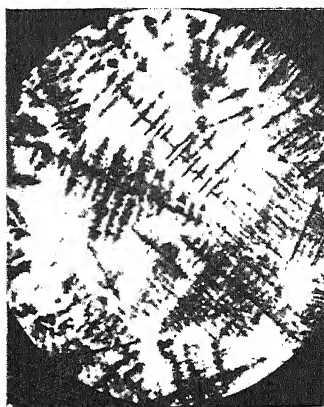


FIG. 7.—Wollastonite-cristobalite eutectic formed in a bottle-glass composition by much slower cooling than in Fig. 6. Crossed nicols. The background is wollastonite which is highly birefringent, and the specimen consisted of alternate layers of wollastonite and cristobalite. $\times 30$.

[See page 214.]

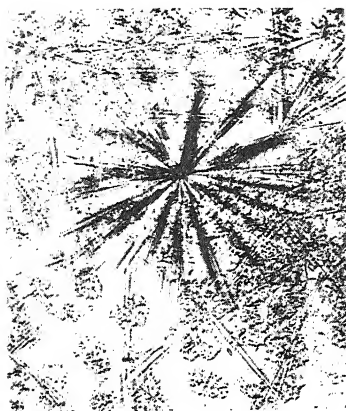


FIG. 8.—Devitrite-tridymite eutectic formed at the glass-air interface in a sheet-glass composition heated for 1.5 hours at 800°. $\times 325$.

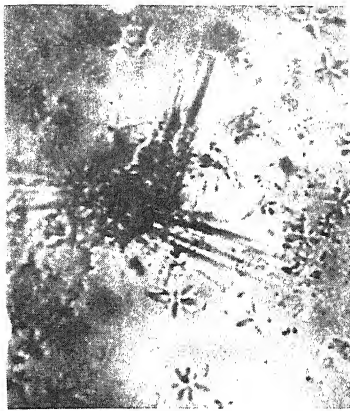


FIG. 9.—Devitrite-christobalite eutectic formed in the body of the glass heated under the same conditions as for Fig. 8. $\times 325$.

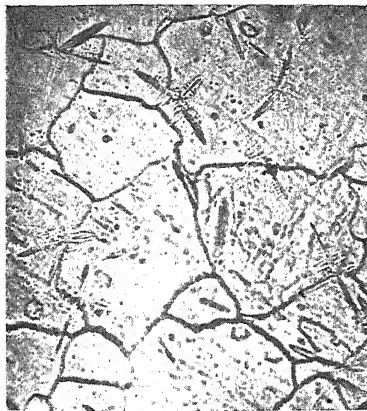


FIG. 10.—Eutectic silica separation of cristobalite dendrites at the interface of glass and platinum alloy container. Note that of the eight dendrites visible, seven of them have commenced growth at a metal grain boundary, where the glass-metal discontinuity is greatest. $\times 325$.

[See page 214.]

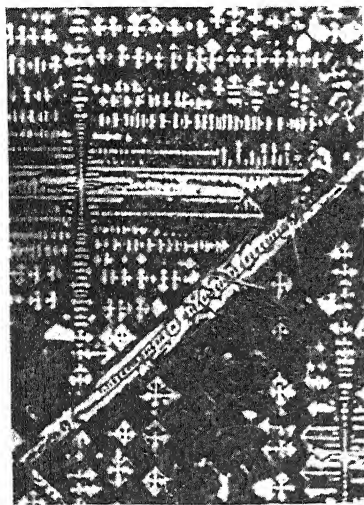


FIG. 12.—Cristobalite dendrite formed in the cooling of an acid open-hearth furnace slag. (After Whiteley and Hallimond.) $\times 15$.



FIG. 13.—Cristobalite dendrite formed in the cooling of a bottle-glass composition very much more viscous than the slag of Fig. 12. (After Holland and Preston.) $\times 250$.

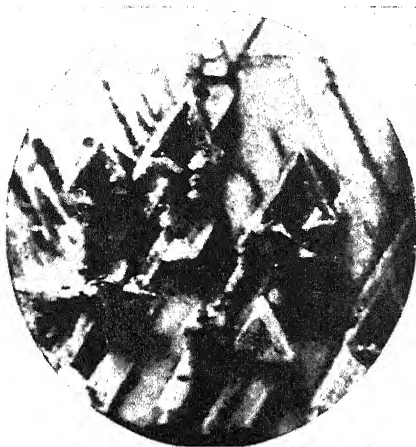


FIG. 14.—Skeleton cristobalite crystals formed on surface of acid slag. (After Whiteley and Hallimond.) $\times 15$.



FIG. 15.—Skeleton cristobalite crystal formed in a bottle-glass composition. (After Holland and Preston.) $\times 500$.

[See page 215.]

THERMODYNAMIC FUNCTIONS OF CARBON SUBOXIDE.

By H. W. THOMPSON.

Received 9th December, 1940.

The ultra-violet absorption spectrum of carbon suboxide has been measured by Thompson and Healey,¹ the Raman spectrum by Engler and Kohlrausch,² and the infra-red absorption spectrum by Lord and Wright.³ These various measurements provide values for the vibration frequencies of the molecule, from which Thompson and Linnett⁴ calculated the stretching force constants. The molecular structure has been studied by the method of electron diffraction by Brockway and Pauling,⁵ and by Boersch.⁶ Examination of the combined spectroscopic and structural data suggests that they are sufficiently accurate for a satisfactory calculation of the thermodynamic functions.

The electron diffraction measurements show that the molecule is linear, and the most probable bond lengths are $r_{cc} = 1.29$ A, $r_{co} = 1.20$ A, which gives $I = 395.2 \times 10^{-40}$ g.cm.². For the linear polyatomic molecule at moderately high temperatures the total translational plus rotational entropy is given by

$$S = R \ln f + RT \frac{d \ln f}{dT}$$

$$\text{in which } f = f_{\text{transl.}} f_{\text{rot.}} = \frac{(2\pi M)^{\frac{3}{2}} \cdot k^{\frac{5}{2}} T^{\frac{5}{2}}}{h^3 \cdot P \cdot N^{\frac{3}{2}}} \cdot \frac{8\pi^2 I \cdot kT}{\sigma}$$

In these partition functions (f), P is the pressure in atmospheres, M the molecular weight in grams, N the Avogadro number, T the absolute temperature, I the moment of inertia, k the Boltzmann constant, h Planck's constant, and σ the symmetry number ($\sigma = 2$).

Thus, using the values of the fundamental constants from International Critical Tables, the total translational plus rotational entropy in the standard state of one atmosphere is given by

$$S^0_{\text{t.r.}} = 7/2 R \ln T + 3/2 R \ln M + R \ln I - R \ln \sigma - 7.63$$

in which M is the molecular weight in grams, and I is expressed in units 10^{-40} g.cm.². The total translational plus rotational contribution to the free energy function $(G^0 - E_0^0)/T$ is given by $(-S^0_{\text{t.r.}} + 6.954)$, and the corresponding contribution to the heat content and specific heat at constant pressure will be $6.954 T$ and 6.954 cal. respectively.

There are seven normal vibrations, the form and assignment of which

¹ *Proc. Roy. Soc., A*, 1936, 157, 331.

² *Z. physikal. Chem., B*, 1936, 34, 214.

³ *J. Chem. Physics*, 1937, 5, 642.

⁴ *Nature*, 1937, 140, 1065.

⁵ *Proc. Nat. Acad. Sci.*, 1933, 19, 860.

⁶ *Wien. Ber.*, 1935, 144, 11b, 1.

have been discussed in the papers referred to above. Four are valency vibrations of the molecular chain (two symmetric and two antisymmetric) and three are doubly degenerate perpendicular vibrations, two being antisymmetric and one symmetric to the centre of symmetry. The values 2200, 843, 2290 and 1570 cm^{-1} can be assigned with certainty to the four valency vibrations. The most satisfactory values for the frequencies of the three degenerate vibrations are 586, 550 and 200 cm^{-1} . The only real ambiguity concerns the value of 550, but the infra-red data of Lord and Wright make it more probable than any other, and taken together the three values are consistent with what might be expected both from a consideration of the spectra of carbon suboxide itself and of the vibration frequencies of molecules involving similar links.

In calculating the thermodynamic contributions, the vibrations have been assumed to be harmonic; the necessary functions have been tabulated by Gordon and Barnes,⁷ and by Wilson.⁸

The total translational plus rotational entropy is then given by

$$S^0_{t,r.} = 7/2R \ln T + 15.46.$$

A summary of the remainder of the calculations is given in Table I.

TABLE I.

°K.	Entropy.			$-(G^0 - E_0^0)/T.$		$(H^0 - E_0^0)/T.$	$(H^0 - E_0^0).$	$C_p^0.$
	Transl. Rot.	Vib.	Total $S^0.$	Vib.	Total.			
279.26	54.63	5.96	60.59	2.23	49.91	3.73	2.98	15.24
298.16	55.09	6.53	61.62	2.49	50.63	4.04	3.28	15.72
300	55.13	6.56	61.69	2.50	50.68	4.06	3.30	15.76
350	56.20	8.03	64.23	3.20	52.45	4.82	4.12	16.85
400	57.13	9.41	66.54	3.89	54.06	5.52	4.99	17.75
450	57.95	10.70	68.65	4.57	55.56	6.13	5.88	18.51
500	58.70	11.96	70.66	5.25	57.00	6.71	6.83	19.19
550	59.34	13.17	72.51	5.92	58.31	7.25	7.81	19.8
600	59.95	14.55	74.50	6.76	59.76	7.78	8.84	20.4
650	60.51	15.47	75.98	7.26	60.82	8.21	9.85	20.9
700	61.02	16.58	77.60	7.91	61.98	8.67	10.94	21.3
750	61.50	17.50	79.00	8.48	63.02	9.02	11.99	21.7
800	61.95	18.42	80.37	9.04	64.04	9.37	13.07	22.1
900	62.77	20.29	83.01	10.22	66.03	10.07	15.32	22.8
1000	63.51	21.92	85.43	11.27	67.83	10.65	17.61	23.3

In Table I the units are cal., degrees Centigrade, moles, except for the total heat content which is given in kcal. per mole.

Attempts to express the various thermodynamic quantities as functions of temperature by means of equations involving four or five constants have been made by several workers, notably by Murphy,⁹ who was able to use data corresponding to those of Table I in constructing expressions for the entropy, free energy, etc., involving the same constants. Murphy's calculations related almost exclusively to diatomic and very simple polyatomic molecules. In the case of more complex molecules where

⁷ *J. Chem. Physics*, 1933, 1, 692.

⁸ *Chem. Rev.*, 1940, 27, 17.

⁹ *J. Chem. Physics*, 1937, 5, 637.

vibrational contributions form a greater part of each thermodynamic function, the form of the expressions given by Murphy may need modification. Such emendations have been discussed in special cases.¹⁰ It has not so far been possible to obtain satisfactory functions in the present case of carbon suboxide, but it is hoped shortly to discuss this in connection with the corresponding expressions for a series of other polyatomic molecules of different types for which the thermodynamic functions have been calculated.

According to Klemenc, Wechsburg and Wagner,¹¹ the equilibrium constant K_p for the reaction $C_3O_2 = CO_2 + C_2$ at 473° K. is of the order 10^{-7} . There is insufficient thermochemical data for us to estimate ΔE_0^0 , and hence ΔG^0 for this reaction, and check the value of K_p .

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¹⁰ See Kassel, *J. Am. C. S.*, 1934, 56, 1838; Linnett and Avery, *J. Chem. Physics*, 1938, 6, 691.

¹¹ *Z. physikal. Chem.*, A, 1934, 170, 97.

THERMODYNAMIC FUNCTIONS AND EQUILIBRIA OF FORMALDEHYDE, DEUTEROFORMALDE- HYDE, PHOSGENE AND THIOPHOSGENE.

By H. W. THOMPSON.

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Beach and Stevenson¹ have calculated the thermodynamic functions of formaldehyde and phosgene, using the spectroscopic data available at the time for the molecular vibration frequencies. The Raman spectrum of thiophosgene was recently measured,² and the vibration frequencies deduced from it have now been correlated with those suggested by an analysis of one system of bands in the ultraviolet absorption spectrum. Details of the latter analysis will be published separately in a forthcoming paper. The structure of thiophosgene has been established by the method of electron diffraction by Brockway, Beach and Pauling,³ so that it is now possible to complete the series by estimating the thermodynamic functions of thiophosgene. In addition, however, the vibration frequencies of formaldehyde and deuterioformaldehyde have now been measured more accurately by Ebers and Nielsen,⁴ and the new values lead to values of the free energy differing appreciably at higher temperatures from those calculated by Beach and Stevenson. The functions for these molecules have therefore been re-calculated. Further, Beach and Stevenson were unable to estimate the contribution to the various functions from the sixth fundamental of phosgene, which moreover being the smallest frequency in magnitude, contributes most to the vibrational partition function. A comparison of the vibration frequencies of phosgene and thiophosgene makes it possible to estimate the sixth phosgene fundamental with reasonable accuracy, and the functions for this molecule too have therefore been re-calculated, using

¹ *J. Chem. Physics*, 1938, 6, 25, 108, 341.

³ *J. Am. Chem. Soc.*, 1935, 5, 2693.

² *Ibid.*, 748.

⁴ *J. Chem. Physics*, 1938, 6, 311.

the more accurate values for the remaining fundamentals found in the infra-red spectrum by Bailey and Hale.⁵

In computing the vibrational contributions, harmonic character has been assumed, and the tables of Gordon and Barnes,⁶ and of Wilson,⁷ were used. When the appropriate anharmonic factors are known, small corrections can at once be made by the method of Gordon and Barnes. The size and significance of such corrections is discussed in special cases below. Beach and Stevenson have considered the error incurred by neglecting the existence of isotopic molecules in the case of the chlorine compounds, and have shown that these errors are certainly not greater than other inaccuracies involved. A mean atomic weight has therefore been assumed in these cases. In order to preserve uniformity with other workers in this field, some of whose data are used below, the fundamental constants used are those given in the International Critical Tables. If the new values of Dunnington⁸ are used, the value for the sum translational and rotational entropy is diminished by about 0.05 units and the vibrational contributions to the various functions are also slightly modified; but these changes will hardly affect the main conclusions about the equilibria discussed.

For each of the molecules involved, the total translational plus rotational entropy of the ideal gas in the standard state of one atmosphere is given by

$$S_{t,r}^0 = 3/2R \ln M - R \ln \sigma + 4R \ln T + \frac{1}{2}R \ln ABC - 9.155$$

in which M is the molecular weight in grams, A , B , and C are the three moments of inertia in units 10^{-40} g.cm.², and σ the symmetry number is 2. The free energy function $(G^0 - E_0^0)/T$ for translation plus rotation is given by $(4R - S_{t,r}^0)$ and the heat content function for translation plus rotation $(H^0 - E_0^0)/T$ by $4R$. The values of the entropy are, of course, of the 'virtual' entropy, and do not include spin contributions.

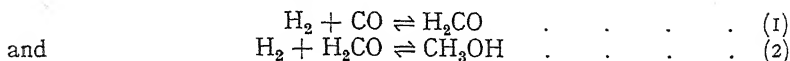
1. Formaldehyde.

According to Dieke and Kistiakowsky,⁹ the moments of inertia are 2.94, 21.39 and 24.33×10^{-40} g.cm.². The vibration frequencies given by Ebers and Nielsen are 1165, 1278, 1503, 1750, 2780 and 2875.

The total translational plus rotational entropy $S_{t,r}^0$ is given by $(4R \ln T + 6.899)$.

The calculations are summarised in Table I.

The equilibrium constants of the reactions



have been measured by Newton and Dodge.¹⁰ Their results do not agree very well with those of other workers, but most probable values are

said to be $K_p = \frac{p_{\text{H}_2\text{CO}}}{p_{\text{H}_2} \cdot p_{\text{CO}}} = 1.72 \times 10^{-5}$ at 520° K for (1), and

$$K_p = \frac{p_{\text{CH}_3\text{OH}}}{p_{\text{H}_2} p_{\text{H}_2\text{CO}}} = 2.09 \times 10^3 \text{ at } 470^\circ \text{ K for (2).}$$

⁵ *Phil. Mag.*, 1938, 25, 98.

⁷ *Chem. Rev.*, 1940, 27, 27.

⁹ *Physic. Rev.*, 1934, 45, 4.

¹⁰ *J. Am. Chem. Soc.*, 1933, 55, 4758; see also Landolt-Börnstein Tabellen.

⁶ *J. Chem. Physics*, 1933, 1, 692.

⁸ *Bull. Amer. Physic. Soc.*, 1939, 14 (i), 17.

TABLE I.*

°K.	Entropy.			$-(G^0 - E_0^0)/T.$		$(H^0 - E_0^0)/T.$ Vib.	$(H^0 - E_0^0).$	$C_{vib}.$	$C_p^0.$
	$S_{c.t.r.}^0$	$S_{vib.}^0$	S_{total}^0	Vib.	Total.				

(i) Formaldehyde.

291·16	52·000	0·084	52·084	0·012	44·064	0·072	2·335	0·45	8·40
298·16	52·189	0·095	52·284	0·013	44·254	0·081	2·393	0·50	8·45
300	52·238	0·099	52·337	0·014	44·304	0·085	2·410	0·52	8·47
350	53·464	0·208	53·672	0·033	45·549	0·174	2·841	0·93	8·88
400	54·525	0·364	54·889	0·065	46·642	0·299	3·299	1·42	9·37
450	55·461	0·560	56·021	0·108	47·621	0·452	3·780	1·95	9·90
470·16	55·807	0·649	56·456	0·129	47·988	0·519	3·981	2·17	10·11
500	56·322	0·795	57·117	0·165	48·539	0·630	4·289	2·49	10·44
520·16	56·610	0·898	57·508	0·192	48·854	0·706	4·502	2·72	10·66
550	57·057	1·055	58·112	0·233	49·342	0·822	4·823	3·03	10·98
600	57·748	1·345	59·093	0·315	50·115	1·030	5·386	3·55	11·50
650	58·385	1·668	60·053	0·409	50·846	1·259	5·920	4·12	12·07
700	58·974	1·968	60·942	0·505	51·531	1·462	6·587	4·53	12·48
800	60·035	2·623	62·658	0·726	52·813	1·897	7·076	5·41	13·36
900	60·971	3·323	64·294	0·981	54·004	2·340	9·258	6·19	14·13
1000	61·809	4·010	65·819	1·250	55·111	2·758	10·707	6·86	14·80
1100	62·566	5·117	67·683	1·527	56·145	3·153	11·101	7·43	15·38
1200	63·258	5·448	68·706	1·869	57·179	3·579	11·527	7·97	15·92
1300	63·894	6·002	69·896	2·116	58·062	3·887	11·835	8·36	16·31
1400	64·484	6·637	71·121	2·417	58·953	4·221	12·169	8·73	16·68
1500	65·036	7·251	72·287	2·719	59·807	4·532	12·480	9·05	17·00

(ii) Deuteroformaldehyde.

298·16	53·311	0·263	53·574	0·044	45·407	0·219	2·380	1·09	9·04
298·16	53·500	0·290	53·790	0·050	45·602	0·240	2·442	1·18	9·13
300	53·549	0·293	53·842	0·051	45·652	0·243	2·457	1·19	9·14
350	54·775	0·529	55·304	0·102	46·929	0·427	2·931	1·84	9·79
400	55·836	0·819	56·655	0·173	48·064	0·646	3·438	2·51	10·4
450	56·772	1·151	57·923	0·263	49·097	0·890	3·977	3·17	11·12
500	57·633	1·424	59·057	0·370	50·055	1·153	4·550	3·81	11·76
550	58·368	1·911	60·279	0·492	50·912	1·419	5·152	4·43	12·37
600	59·059	2·323	61·382	0·628	51·739	1·696	5·786	5·00	12·95
650	59·696	2·806	62·502	0·799	52·547	2·006	6·470	5·58	13·53
700	60·285	3·220	63·505	0·979	53·316	2·241	7·132	6·03	13·98
800	61·346	4·034	65·380	1·266	54·664	2·768	8·573	6·90	14·84
900	62·281	4·882	67·164	1·619	55·953	3·263	10·090	7·61	15·56
1000	63·120	5·719	68·839	1·987	57·159	3·732	11·680	8·21	16·16
1100	63·877	6·552	70·429	2·381	58·310	4·171	13·332	8·72	16·66
1200	64·569	7·311	71·880	2·748	59·369	4·563	15·013	9·12	17·07
1300	65·205	8·052	73·257	3·130	60·387	4·922	16·710	9·46	17·41
1400	65·795	8·760	74·555	3·503	61·350	5·258	18·488	9·74	17·69
1500	66·347	9·447	75·794	3·881	62·280	5·566	20·271	10·02	17·97

(iii) Thiophosgene.

291·16	64·188	5·625	69·811	2·099	58·33	3·526	3·341	7·380	15·33
298·16	64·377	5·813	70·19	2·189	58·62	3·624	3·451	7·502	15·45
300	64·426	5·850	70·28	2·207	58·69	3·643	3·477	7·531	15·48
350	65·052	7·078	72·73	2·820	60·53	4·258	4·245	8·254	16·20
400	66·713	8·212	74·93	3·420	62·19	4·792	5·096	8·732	16·68
450	67·649	9·272	76·92	4·008	63·71	5·264	5·950	9·291	17·24
500	68·490	10·280	78·77	4·590	65·13	5·690	6·819	9·639	17·59
550	69·145	11·223	80·47	5·155	66·45	6·068	7·700	9·971	17·92
600	69·936	12·113	82·05	5·707	67·70	6·406	8·612	10·223	18·17
650	70·573	13·409	83·98	6·530	69·16	6·879	9·640	10·507	18·45
700	71·162	13·704	84·87	6·726	69·94	6·977	10·447	10·603	18·55
800	72·223	15·140	87·36	7·691	71·96	7·449	12·318	10·880	18·83
900	73·159	16·443	89·60	8·601	73·81	7·842	14·211	11·074	19·02
1000	73·997	17·602	91·60	9·436	75·49	8·166	16·114	11·221	19·17

* The various units are cal., degrees Centigrade, moles, except for $(H^0 - E_0^0)$ which is measured in kcal. per mole.

TABLE I.—Continued.

°K.	Entropy.			$-(G^0 - E_0^0)/T$.		$(H^0 - E_0^0)/T$.	$(H^0 - E_0^0)$.	C_{vib} .	C_p^0 .
	$S_{t.r.}^0$	S_{vib}^0	S_{total}^0	Vib.	Total.	Vib.			
(iv) Phosgene.									
291·16	64·158	4·654	68·81	1·675	57·89	2·979	3·182	6·45	14·40
298·16	64·347	4·823	69·17	1·755	58·16	3·069	3·285	6·57	14·51
300	64·396	4·859	69·26	1·774	58·22	3·085	3·310	6·58	14·53
350	65·622	5·926	71·55	2·289	59·97	3·638	4·055	7·27	15·21
400	66·683	6·932	73·61	2·806	61·53	4·127	4·830	7·82	15·77
450	67·619	7·878	75·50	3·319	62·99	4·559	5·628	8·28	16·22
500	68·480	8·769	77·25	3·819	64·35	4·950	6·449	8·66	16·61
550	69·215	9·609	78·82	4·305	65·56	5·304	7·289	9·00	16·95
600	69·906	10·412	80·32	4·786	66·75	5·616	8·138	9·29	17·23
650	70·543	11·155	81·70	5·240	67·84	5·915	9·011	9·54	17·49
700	71·132	11·872	83·10	5·691	68·87	6·181	9·890	9·76	17·71
750	71·680	12·557	84·24	6·134	69·87	6·423	10·778	9·95	17·90
800	72·193	13·211	85·40	6·558	70·82	6·650	11·680	10·12	18·07
850	72·675	13·825	86·50	6·962	71·69	6·862	12·588	10·28	18·23
900	73·129	14·566	87·70	7·463	72·65	7·093	13·537	10·43	18·38
1000	73·967	15·523	89·49	8·118	74·14	7·405	15·353	10·64	18·59

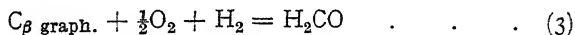
Now using the heats of formation given by Bichowsky and Rossini,¹¹ for reaction (1) at 291·16° K we have $-\Delta H = 28·70 - 26·84 = 1·86$ kcal. The values of $(H^0 - E_0^0)$ at this temperature for hydrogen, carbon monoxide, and formaldehyde are 1·975, 2·024, and 2·335 kcal. Thus $\Delta(H^0 - E_0^0) = 1·664$ kcal., and hence for reaction (1) $\Delta E_0^0 = -0·20$ kcal. The values of $-(G^0 - E_0^0)/T$ for hydrogen,¹² carbon monoxide,¹³ and formaldehyde at 520° K. are 28·237, 44·228 and 48·854 cal, whence $\Delta(G^0 - E_0^0) = 12·27$ kcal., so that $\Delta G^0 = -RT \ln K_p = 12·07$ and $K_p = 0·83 \times 10^{-5}$. The difference between this and the measured value is within the possible experimental error, but alternatively may well arise from the use of an inaccurate value for the heat of formation of formaldehyde. It may be preferable to reverse the procedure and calculate ΔE_0^0 from the measured value of K_p . Thus $\Delta G_{520}^0 = -RT \ln K_p = 11·34$, and $\Delta E_0^0 = -0·96$ kcal.

For the purpose of similar computations on reaction (2) it is necessary to have the thermodynamic functions of methyl alcohol. These have been discussed by several workers,¹⁴ but correct values are still lacking because of the uncertainty of the potential barrier to internal torsion about the C—O bond. Kassel calculated the free energy on the assumption of both unrestricted and completely restricted internal rotation. It is now certain that the true value lies between these limits, and it is probable that the potential barrier is about 2000 cal. Using this value, and estimating the torsional contribution by the method of Pitzer,¹⁵ the function has now been recalculated. The moments of inertia and fundamental frequencies used were those recently determined by Borden and Barker,¹⁶ namely, $I_1 = 6·8$, $I_2 = 33·83$, and $I_3 = 35·18$

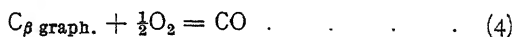
¹¹ *Thermochemistry* (Rheinhold), 1936.¹² Giauque, *J. Am. Chem. Soc.*, 1930, **52**, 4826.¹³ *Ibid.*, 1932, **54**, 2622; 1933, **55**, 5071.¹⁴ Halford and Pecherer, *J. Chem. Physics.*, 1938, **6**, 571; Kassel, *ibid.*, 1936, **4**, 493.¹⁵ *Ibid.*, 1937, **5**, 469.¹⁶ *Ibid.*, 1938, **6**, 553.

$\times 10^{-40}$, with frequencies 3683, 2978 (2), 2845, 1477, 1455, 1405, 1340, 1230, 1107, and 1034. The reduced moment about the C—O bond was taken to be 1.16×10^{-40} g.cm.². It is unlikely that the refinements introduced by a more precise value of the potential barrier, or by the more elaborate theory of torsion of Crawford,¹⁷ will appreciably affect the main conclusions of the present computations. Thus at 291.16° K. the functions $(H^0 - E_0^0)$ for hydrogen, formaldehyde, and methyl alcohol are 1.975, 2.335 and 2.618 kcal., so that for the reaction (2), $\Delta(H^0 - E_0^0) = -1.692$ kcal. Now using the heats of formation given by Bichowsky and Rossini, at the same temperature $-\Delta H = 19.74$ kcal., so that $\Delta E_0^0 = -18.05$ kcal. At 470° K. the free energy functions $-(G^0 - E_0^0)/T$ for hydrogen, formaldehyde and methyl alcohol are 27.545, 47.988 and 52.365, whence $\Delta(G^0 - E_0^0) = 10.88$ kcal., and using the above value of ΔE_0^0 , $\Delta G^0 = -RT \ln K_p = -7.17$. Thus $K_p = 2.14 \times 10^3$; the measured value is 2.09×10^3 .

We may now consider the formation of formaldehyde from its elements

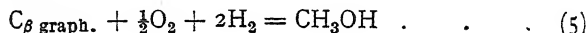


It was seen above for the reaction (1), $\Delta E_0^0 = -0.20$ kcal. (from heats of combustion and thermodynamic functions), and -0.96 kcal. (from equilibrium constant and thermodynamic functions), the mean being -0.58 kcal. According to Kassel,¹⁸ we also have $\Delta E_0^0 = -27.40$ kcal. for the reaction



Adding, it follows that for reaction (3) $\Delta E_0^0 = -27.98$ kcal.

Also for the process



taking the heats of formation from Bichowsky and Rossini, at 18° C. we have $\Delta H = -48.22$ kcal.; at this temperature $\Delta(H^0 - E_0^0) = -2.83$ whence $\Delta E_0^0 = -45.39$ kcal. Combining this result with the value $\Delta E_0^0 = -18.05$ kcal. for the process (2), it follows that for process (3), $\Delta E_0^0 = -27.34$ kcal. Thus a mean of two close values for this quantity is -27.7 kcal. A third estimate can be made by combining heat of formation data with values of $(H^0 - E_0^0)$ for β graphite, hydrogen, oxygen and formaldehyde. Thus for process (3), at 18° C., $\Delta H = -28.48$ kcal., $\Delta(H^0 - E_0^0) = 0.89$, whence $\Delta E_0^0 = -27.59$, which agrees well with the previous value.

Adopting the value $\Delta E_0^0 = -27.7$ kcal. for the process (3), the free energy of formation has been calculated, using values of the free energy of β graphite, hydrogen and oxygen from the work of Giauque,¹⁹ and Johnston and Walker.²⁰ The results are summarised in

TABLE II.

T(°K.).	ΔG^0 .
298.16	-27.17
300	-27.16
350	-26.9
400	-26.6
450	-26.3
500	-26.0
550	-25.6
600	-25.2
650	-24.8
700	-24.4
800	-23.6
900	-22.7
1000	-21.9
1100	-21.0
1200	-20.15
1300	-19.2
1400	-18.25
1500	-17.3

¹⁷ J. Chem. Physics, 1940, 8, 273, 744.

¹⁸ J. Am. Chem. Soc., 1934, 56, 1838.

¹⁹ Ibid., 1932, 54, 2622.

²⁰ Ibid., 1933, 55, 712.

Table II. ΔF^0 is the free energy of formation in kcal. per mole of the ideal gas at one atmosphere pressure.

2. Deuteroformaldehyde.

The structure assumed is that of formaldehyde with $r_{\text{CH}} = 1.09$, $r_{\text{CO}} = 1.21$ A, and $\text{HCH} = 120^\circ$, giving values for the moments of inertia 5.88, 25.52 and 31.42×10^{-40} g.cm.². The total translational plus rotational entropy of the ideal gas in the standard state of one atmosphere is given by $S_{\text{t.r.}}^0 = 4R \ln T + 8.210$. The vibration frequencies determined by Ebers and Nielsen are 938, 990, 1106, 1700, 2056 and 2160 cm.⁻¹.

The entire calculations are summarised in Table I (ii). The heat of formation of deuteroformaldehyde has not been measured and there are no experimental data on equilibria from which further calculations such as were possible with formaldehyde can be made.

3. Thiophosgene.

According to Brockway, Beach and Pauling,²¹ $r_{\text{CS}} = 1.63$ A, $r_{\text{CCl}} = 1.70$ A, and $\angle \text{Cl-C-Cl} = 116^\circ$, from which the moments of inertia assuming a mean atomic weight for chlorine are 74.1, 244.5 and 318.6×10^{-40} g.cm.². The Raman spectrum of the liquid was previously described.²² Using the vibration frequencies deduced from it, together with the rules of Herzberg and Teller,²³ one system of bands in the ultraviolet absorption spectrum of the vapour has now been analysed, and suggests the following fundamentals: 1140, 660, 500, 365, 290 and 200 cm.⁻¹.

The total translational plus rotational entropy in the standard state of one atmosphere for the ideal gas is then $S_{\text{t.r.}}^0 = (4R \ln T + 19.09)$ cal. per degree per mole. The remainder of the calculations are collected in Table I (iii).

With a molecule having comparatively low vibration frequencies the vibrational contributions to the various functions are considerable, and small inaccuracies in the values of the fundamentals are therefore more pronounced, especially at higher temperatures. Values have for this reason only been given to 1000° K. In the same way the anharmonicity error might be expected to be more noticeable here than with the molecules previously discussed. The analysis of the ultraviolet system suggests that for several of the vibrations, the successive quanta diminish by roughly 1 per cent. The effect of this upon the several thermodynamic quantities can be estimated from the tables of Gordon and Barnes. In their nomenclature x is approximately 0.005 and at 300° K. the values given in Table I (iii) for S^0 , $-(G^0 - E_0^0)/T$ and C_p^0 will be increased by approximately 0.12, 0.05 and 0.15 cal.; at 1000° K. the differences will be about 0.4, 0.2 and 0.45 cal. These small differences, although important, would probably not materially affect calculations of equilibria, but since neither the heat of formation of thiophosgene nor other relevant thermal data are available, such calculations cannot be made.

²¹ *J. Am. Chem. Soc.*, 1935, **57**, 2693.

²² *J. Chem. Physics.*, 1938, **6**, 748

²³ *Z. physikal. Chem.*, B, 1933, **21**, 410.

4. Phosgene.

The molecular structure has been determined by Brockway, Beach and Pauling, who give $r_{\text{CCl}} = 1.68 \text{ \AA}$, $r_{\text{CO}} = 1.28 \text{ \AA}$, and $\text{Cl}-\hat{\text{C}}-\text{Cl} = 117^\circ$, from which the moments of inertia are 104.8, 241.8 and $346.6 \times 10^{-40} \text{ g.cm}^2$. Early measurements of the spectra included those of Marton²⁴ (infra-red), Henri and Howell²⁵ (ultraviolet), and Dadiou and Kohlrausch²⁶ (Raman). More recently Ananthakrishnan²⁷ has re-measured the Raman spectrum including a study of the depolarisation factors, while Bailey and Hale²⁸ have analysed the infra-red spectrum between 1.20μ . These investigations establish definitely the values of five fundamentals, namely the three symmetrical vibrations of frequency 1827, 570, 302 cm^{-1} , and the two planar antisymmetric vibrations of magnitude 845 and 444. The sixth fundamental, which is the non-planar deformation, cannot be fixed unambiguously from the infra-red data, but it can be estimated very satisfactorily by comparing the vibration frequencies of phosgene and thiophosgene. The figures of Table III show that the sixth fundamental of phosgene will lie close to 230 cm^{-1} .

TABLE III.

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Thiophosgene	1140	500	290	660	365	200
Phosgene	1827	570	302	845	444	(230)

The total translational plus rotational entropy for the ideal gas at one atmosphere is then $S^0_{\text{t.r.}} = (4R \ln T + 19.06) \text{ cal. per degree per mole}$. In view of later considerations it may be noted that the possible error in the moments of inertia cannot lead to an error in $S^0_{\text{t.r.}}$ of more than $\pm 0.08 \text{ cal.}$, and the probable error is much less than this.

The entire calculations are summarised in Table I (iv).

No direct measurements are available for the specific heat of phosgene, and the entropy has not therefore been determined experimentally. Fink and Bonilla²⁹ estimated the specific heat at 25°C . by interpolation but their result cannot be regarded as satisfactory. The molar specific heat of carbon dioxide (C_p^0) at 25°C . is calculated statistically to be 9.05 cal., that of carbon tetrachloride (frequencies 459, 775 (3), 313 (3) and 217 (2)) is 19.94 cal. The arithmetic mean is 14.50 cal., and the agreement with the value of 14.51 given above for phosgene is therefore excellent; it is accidental, however, that such a simple linear interpolation, even for qualitative purposes, leads to the correct value.

If the vapour is assumed to obey the Berthelot equation of state, it follows that $C_p - C_p^0 = \frac{81}{32} \cdot R \cdot (T_c/T)^3 (P/P_c)$. According to German and Taylor,³⁰ the critical values are $T_c = 182^\circ \text{C}$., $P_c = 56 \text{ atmos.}$

²⁴ *Z. physikal. Chem.*, 1925, **117**, 97.

²⁵ *Proc. Roy. Soc., A*, 1930, **128**, 190.

²⁶ *Wien. Ber.*, 1930, **139**, 717; *Z. physikal. Chem., B*, 1934, **27**, 176.

²⁷ *Proc. Ind., Acad.*, 1937, **5**, 285.

²⁸ *Phil. Mag.*, 1938, **25**, 98.

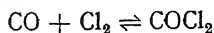
²⁹ *J. phys. Chem.*, 1933, **37**, 1135.

³⁰ *J. Am. Chem. Soc.*, 1926, **48**, 1154.

Thus at 25° C. and one atmosphere, C_p for the real vapour will be 14.8 cal. Also for the entropy $S = S^0 - \frac{27}{32} R(T_0/T)^3(P/P_0)$ so that at 25° C. the entropy of the real vapour will be 69.02 cal. per degree per mole.

The statistical calculation of C_p can involve only two sources of error, namely that introduced by an incorrect value of the sixth fundamental, and that arising from vibrational anharmonicity. At moderate temperatures these are unlikely to lead to an error of more than 0.1 cal. per mole.

The thermal equilibrium



has been measured several times, but the data are rather unsatisfactory. We may nevertheless examine how closely the measured equilibrium

TABLE IV.

t° C.	K_p .	Observer.
300	656	H.
314	329.5	A.H.P.
341	176.8	A.H.P.
373.3	43.6	B.P.
394.6	22.6	B.P.
400	24.5	H.
400	20.8	A.H.P.
406	32.0	A.H.P.
413.5	12.7	B.P.
443	9.34	A.H.P.
449	7.65	A.H.P.
451.3	4.16	B.P.
460	6.76	A.H.P.
486	4.765	A.H.P.
500	2.3	H.
503	1.23	B.D.
505	2.63	A.H.P.
553	0.56	B.D.
603	0.21	B.D.

constants agree with those calculated from the free energy data which are now available for the three molecules involved.

Table IV summarises values of $K_p = \frac{P_{\text{CO}}P_{\text{Cl}_2}}{P_{\text{COCl}_2}}$, the units of pressure being one atmosphere, calculated from the data of Bodenstein and Dunant ³¹ (B. and D.), Bodenstein and Plaut ³² (B. and P.), Horak ³³ (H.), and Atkinson, Heycock and Pope ³⁴ (A., H. and P.). Some values of A., H. and P. are so badly out of line that they have been omitted. The data of this table are plotted as $\log K_p$ against $1/T$ in Fig. 1. The data

of Fig. 1 are seen to fall into two sets. Fairly satisfactory straight line plots of $\log K_p$ against $1/T$ can be drawn through the points of B. and D., B. and P., on the one hand (line A), and through those of A.H.P. and H. on the other (line B). These two straight lines differ in slope, giving for line A, $\Delta H = -26300$ cal. and for line B, $\Delta H = -24200$ cal. Values of K_p read off these lines at a series of temperatures are given below in Table V.

Now at 298.16° K. the values of $(H^0 - E_0^0)$ for carbon monoxide, chlorine and phosgene are 2.024, 2.16, 3.182 kcal. per mole. Hence for the reaction $\text{CO} + \text{Cl}_2 = \text{COCl}_2$ we have $\Delta(H^0 - E_0^0) = -1.00$ kcal. According to Bichowsky and Rossini, the heats of formation at 18° C. of phosgene and carbon monoxide are 53.5 and 26.84 kcal., so that $\Delta H = -26.66$ kcal. Hence $\Delta E_0^0 = -25.66$ kcal. Taking

³¹ *Z. physikal. Chem.*, 1908, 61, 437.

³³ *Dissertation*, Berlin. See ref. 32.

³² *Ibid.*, 1924, 110, 399.

³⁴ *J. Chem. Soc.*, 1920, 117, 1410.

for the free energies of chlorine and carbon monoxide the values of Clayton and Giauque,³⁵ and Giauque and Overstreet,³⁶ $\Delta(G^0 - E_0^0)$ can be calculated and hence $\Delta G^0 = -RT \ln K_p$. Table V summarises the data at the selected temperatures.

Column six (1) of Table V gives $-\Delta G^0$ assuming the above value of

TABLE V.

°K.	$-(G^0 - E_0^0)/T$.		Phosgene.	$\Delta(G^0 - E_0^0)$.	$-\Delta G^0$.		K_p .			
	Carbon Monoxide.	Chlorine.			(1).	(2).	(1).	(2).	(A).	(B).
600	45.238	51.298	66.75	17.87	7.79	6.79	664	289	186	252
650	45.801	51.936	67.84	19.43	6.23	5.23	121	56	34	52
700	46.323	52.531	68.87	21.0	4.66	3.66	28	13.7	7.95	13.8
750	46.813	53.089	69.87	22.52	3.14	2.14	8.12	4.2	2.3	4.5
800	47.271	53.614	70.82	24.05	1.61	0.61	2.73	1.46	0.76	1.62
850	47.703	54.110	71.69	25.60	-0.06	-0.94	0.965	0.575	0.28	0.68

$\Delta E_0^0 = -25.66$ kcal., and the seventh column (1) is the corresponding value of K_p . It is seen that the calculated values (line C of Fig. 1) are uniformly much higher than those measured. If the correct plot of

$\log K_p$ against $1/T$ lies between the limits of lines A and B, some reason for the discrepancy must be found. There are two possibilities: (i) incorrect values for the free energies, (ii) an inaccurate value of the heat of formation of phosgene. As regards the former, only the free energy of phosgene can be in doubt. An error here might arise from an incorrect value of the sixth fundamental, from incorrect moments of inertia, or from vibrational anharmonicity. If the anharmonicity coefficients are roughly the same as those of phosgene discussed above, about 0.1 cal.

will have to be added to $-(G^0 - E_0^0)/T$ at 800° K. This means, however, that $\Delta(G^0 - E_0^0)$ for the reaction will be diminished and $-\Delta F^0$ will be increased, giving a slightly larger value of K_p and a bigger

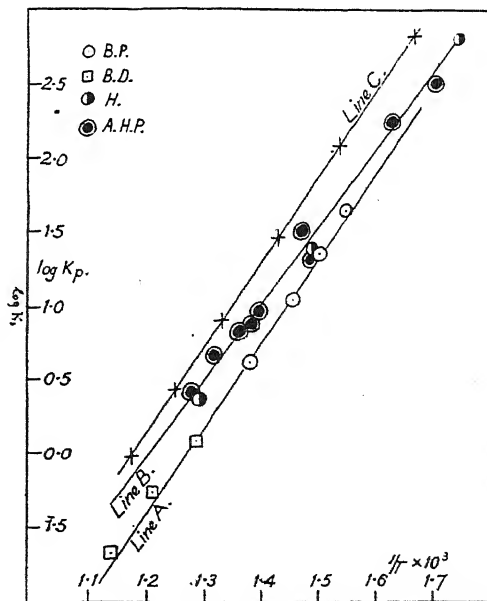


FIG. 1.

³⁵ *J. Am. Chem. Soc.*, 1933, 55, 5071; 1932, 54, 2610.

³⁶ *Ibid.*, 1731.

discrepancy with the measured values. If the moments of inertia are in error the effect will be either to cancel out the anharmonic error, or to enhance it and lead to still greater values of K_p . An error in the value of the sixth fundamental cannot possibly be great enough to bring the calculated and experimental values into agreement. It therefore seems clear that the disparity originates in the use of a high value for the heat of formation of phosgene. The figure of 53.5 kcal.

TABLE VI.

T (°K).	ΔG^0
298.16	-49.25
300	-49.2
350	-48.7
400	-48.2
450	-47.7
500	-47.3
550	-46.8
600	-46.3
650	-45.7
700	-45.4
800	-44.5
900	-43.6
1000	-42.6

given by Bichowsky and Rossini is obtained by laying relative weight on the equilibrium measurements of Bodenstein and Plaut, whose plot of $\log K_p$ against $1/T$ is definitely steeper than that of the other workers, although in fact it would be quite possible to draw a line of smaller slope through their data. Berthelot from combustion data gave 52.7 kcal. per mole as the heat of formation of phosgene. If we assume a value of 52.5 kcal., the calculated values of $-\Delta G^0$ and K_p (Table V, columns six (2) and seven (2)) are seen to fall well into line with those measured. The value for ΔH_{291} for the reaction is then -24.66 kcal., which is within the range of values obtainable from the

variation of equilibrium constant with temperature.

Assuming for the heat of formation the value 52.5 kcal., the free energy of formation of phosgene has been calculated, assuming the free energies of carbon, oxygen, and chlorine of Clayton and Giauque, Johnston and Walker, and Giauque and Overstreet. The results are given in Table VI. At 18° C. $\Delta(H^0 - E_0^0) = -0.23$ kcal., and $\Delta H = -52.28$ kcal. so that $\Delta E_0^0 = -52.05$ kcal.

Summary.

The entropy, free energy, heat content and specific heat of formaldehyde and deuterioformaldehyde have been calculated over a wide range of temperature. The results have been correlated with measurements on the equilibria $H_2 + CO \rightleftharpoons H_2CO$ and $H_2 + H_2CO \rightleftharpoons CH_3OH$. The free energy of formation of formaldehyde between 300-1500° K. has been calculated.

Values have been obtained for the corresponding thermodynamic functions of thiophosgene and phosgene for temperatures 300-1000° K. In the latter case the calculated free energies have been used to calculate the equilibrium constant of the reaction $CO + Cl_2 \rightleftharpoons COCl_2$ over a range of temperature. Comparison of the calculated values with those determined experimentally suggests a better value for the heat of formation of phosgene than that previously assumed. The significance of various possible errors in the calculations has been discussed.

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THE VISCOSITY OF CELLULOSE AND ITS NITRATE IN DILUTE SOLUTION.*

By S. M. NEALE AND R. WAITE.

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Of the various methods that have been employed in attempts to determine the molecular chain length of high molecular substances such as cellulose, only the osmotic pressure, viscosity, and ultra centrifugal methods, and the chemical determination of end groups, have thrown any real light on the subject.¹ Apart from the experimental difficulties, progress is hampered by doubt as to the validity of the theoretical basis for the interpretation of results, where classical methods proved applicable for "normal" substances, are applied to substances whose molecules are known to be highly abnormal in size and shape.

In the case of long chain substances, much use has been made of viscosity in dilute solution as an index of molecular size. The measured quantity is one which increases with the molecular weight, and the apparatus required is relatively simple. On the other hand, the interpretation of the results is almost wholly empirical. It depends either on gross extrapolation from the viscosities of simple homologues of chemically ascertainable chain length, as used by Staudinger,² or comparison with other methods such as ultra centrifugal analysis, as used by Kraemer and Lansing.³

Staudinger and his co-workers have, however, extensively investigated the viscosity method, but in spite of the volume of their published work there appears to be little or no information as to the general technique and the degree of accuracy attained, which has been called in question by Meyer and van der Wyk.⁴

The object of the present work was to determine whether a sufficiently accurate technique for the measurement of the viscosity of cellulose and its derivatives in very dilute solutions could be established, and to examine the validity of the arbitrary simple relations between viscosity and concentration which the above authors have used in the interpretation of their results. The variation of the viscosity with the nature and composition of the solvent was also investigated, as well as its dependence on the rate of shear employed in the viscometer, since almost all the solutions showed anomalous flow.

* Symbols used:—

η_0 = viscosity of solvent.

η = apparent viscosity of solution at an arbitrarily chosen shearing stress of 31.6 C.G.S. units.

$\eta_r = \eta/\eta_0$; $\eta_{sp} = \eta_r - 1$.

c = grams of solute per 100 c.c. of solvent at 20° C.

¹ For a recent survey of progress with cellulose see Neale, *Chem. Ind.*, 1936, 55, 602.

² Staudinger, *Die hochmolekularen organischen Verbindungen*. Springer, Berlin, 1932.

³ Kraemer and Lansing, *J. Physic. Chem.*, 1935, 39, 153.

⁴ Meyer and van der Wyk, *Koll. Z.*, 1936, 76, 278.

Experimental.

Cellulose Material Used.—Since it was not one of the objects of this investigation to attempt to establish values for the "molecular weights" of typical samples of cellulose, only one sample of cellulose was used throughout. This was in the form of a two-fold yarn of 28's count of Sakellaridis cotton, which had received a full technical bleach, consisting of a caustic soda boil at 40 lbs. pressure for 7 hours, then two bleaching treatments with slightly alkaline calcium hypochlorite, followed by a wash with dilute ammonia in the laboratory. The examination of this material showed that it had undergone almost the minimum of degradation:

Copper Number 0.015 (Schwalbe-Braidy method)
 Fluidity (0.5 % solution) 3.8
 COOH value 0.4 milliequiv./100 g.
 Solubility in boiling 1 % NaOH 0.08 % (by wet combustion of soln.).

Description of Apparatus.—Ostwald capillary viscometers were used, fitted with taps at the end of each arm so as to make it possible to handle cellulose solutions with rigid exclusion of oxygen.

Known external pressures could be applied to accelerate the flow by means of a suitable aspirator and water gauge system. The gas used was cylinder hydrogen purified by passage over palladised asbestos always kept at 150° C. During measurements the viscometers were held vertically in a 60 litre thermostat maintained at $20 \pm 0.05^\circ$ C.

The viscometers were carefully selected for uniformity of capillary bore and were calibrated both by dimensional measurement and by the flow of water and of benzyl alcohol ($\eta_{20^\circ} = 0.0621$ poise, determined in viscometers C and D). The times of flow for water were measured again at the end of this research, and had undergone no significant change.

TABLE I.

Visco- meter.	Vol. of Bulb (c.c.).	Length of Capillary (cm.).	Radius of Capillary By Hg Thread.	K_{Hg} $\times 10^4$.	$K_{\text{H}_2\text{O}}$ $\times 10^4$.	$K_{\text{PhCH}_2\text{OH}}$ $\times 10^4$.	Time of Flow H_2O (sec.).
A	2.35	6.07	0.0333	3.39	3.58	3.35	29.6
B	2.46	10.10	0.0319	1.88	1.86	1.91	55.0
C	2.37	10.25	0.0210	0.358	0.358	—	281.6
D	2.29	10.06	0.0210	0.400	0.395	—	259.2

$$K = \frac{\eta}{\rho t} + \frac{mV}{8\pi h^2} = \frac{hg\pi r^4}{8lV} \quad (m = 1.00).$$

Preparation of Cellulose Solutions and Measurement of Viscosity.—A solution of cuprammonium hydroxide was prepared⁶ by the action of air on copper powder suspended in aqueous ammonia and from it, after careful analysis, four solutions of the following compositions were prepared by appropriate dilution, and stored under hydrogen:—

	CuAm I.	CuAm II.	CuAm III.	CuAm IV.
Cu (g./l.)	13.9	9.4	7.2	13.5
NH ₃ (g./l.)	214	211	212	136
HNO ₃ (g./l.)	0.47*	0.35	0.24	0.47
Sucrose (g./l.)	1.0	1.0	1.0	1.0
Viscosity (centipoise)	1.37	1.34	1.31	1.27

* By nitrometer method 0.48 g./l., by KMnO₄ 0.47 g./l.

⁵ Neale and Stringfellow, *Trans. Faraday Soc.*, 1937, 33, 881.

⁶ Clibbens and Geake, *J. Text. Inst.*, T, 1928, 19, 77.

The cotton yarn was cut up into fragments not greater than 1 mm. in length, and weighed in a small copper foil cylinder on an assay balance sensitive to 0.005 mg., the appropriate allowance being made for moisture content, which was determined on parallel samples dried at 110° C. From the cylinder the cotton was transferred to a glass tube which narrowed at the lower end to a capillary and was closed by a piece of rubber tubing and a screw clip. A piece of stainless steel rod was placed in the tube to act as a stirrer, the tube closed, evacuated to 0.1 mm. Hg, and then filled with the cuprammonium solution. The tube was then slowly revolved end over end for 24 hours in a light-tight box to effect stirring, removed, and the solution transferred under pressure of hydrogen through a No. 3 Jena glass filter to the viscometer evacuated to 0.1 mm. Hg. The viscometer was filled up to an etched mark, the taps closed, transferred to the thermostat and connected to the hydrogen pressure system. A series of measurements of times of flow was made at six different pressures for each solution, with two or more measurements at each pressure. If the viscometer was kept covered with a black jacket except during the actual measurement, the viscosity remained constant within less than 1 % even over 24 hours.

From the time of flow and a knowledge of the viscometer constants the applied pressure and the density of the solution, the shearing stress $\frac{Pr}{2l}$ and the corresponding rate of shear $\frac{4V}{\pi r^3 t}$ at the capillary wall were calculated for each value of P , and the logarithms of these quantities were plotted. For the solvents the slope of the line was unity, but for the solutions it was always greater than one, being in fact the " N " value of the empirical equation used by Farrow, Lowe and Neale⁷ to describe the abnormality of flow in a capillary.

$$\left(\frac{Pr}{2l}\right)^N = \eta \frac{(N+3)V}{\pi r^3 t}$$

Thus for a solution the corrected rate of shear at the capillary wall becomes $\frac{(N+3)V}{\pi r^3 t}$, and the apparent viscosity (shearing stress/rate of shear) is a function of the shearing stress itself. It was therefore necessary to choose an arbitrary value of the shearing stress for the comparison of different solutions, and this was taken as $\log_{10} \frac{Pr}{2l} = 1.5$.

Experimental Results.

Cellulose in Cuprammonium Solutions I, II, III and IV.

The viscosities of solutions of similar cellulose contents, but differing in copper and ammonia content as indicated above, are compared in Table II. Each figure is the mean of duplicates in good agreement. The values of η_{sp}/c are plotted in Fig. 1.

Staudinger suggests that η_{sp}/c should be constant for values of η_{sp} within the range 0.02-0.3, but does not give precise experimental data. It is difficult to decide from the present data whether this is so or not, but it is clear that with the high viscosity cellulose used it could only be checked by using solutions so very dilute that quite exceptional experimental precautions would be required. On the

⁷ Farrow, Lowe and Neale, *J. Text. Inst.*, T, 1928, 19, 18.

other hand, it is possible from Fig. 1 to deduce approximate values of $\lim_{c \rightarrow 0} \frac{\eta_{sp}}{c}$, the quantity employed by Kraemer and Lansing.

TABLE II.

Cellulose (g./100 c.c.).	0.	0.025.	0.05.	0.10.	0.20.	0.30.	0.40.	0.50.
η_{sp} {	I	0	0.29	0.56	1.30	3.51	7.31	22.5
	II	0	—	0.48	1.14	3.19	6.35	—
	III	0	—	0.49	1.19	3.67	7.73	28.2
	IV	0	—	0.66	—	4.25	14.0	32.5
η_{sp}/c {	I	—	11.5	11.2	13.0	17.6	24.4	44.9
	II	—	—	9.56	11.4	15.7	21.2	—
	III	—	—	9.9	11.9	18.4	25.8	56.4
	IV	—	—	13.2	—	21.2	35.0	65.0
$(\log \eta_r)/c$ {	I	—	4.39	3.85	3.63	3.27	3.07	2.74
	II	—	—	3.39	3.30	3.07	2.89	—
	III	—	—	3.50	3.41	3.35	3.14	2.91
	IV	—	—	4.41	—	3.60	2.94	3.02
N {	I	1.00	1.01	1.05	1.06	1.10	1.10	1.13
	II	1.00	—	1.02	1.08	1.11	1.13	—
	III	1.00	—	1.03	1.05	1.11	1.14	1.30
	IV	1.00	—	1.04	—	1.09	1.24	1.31

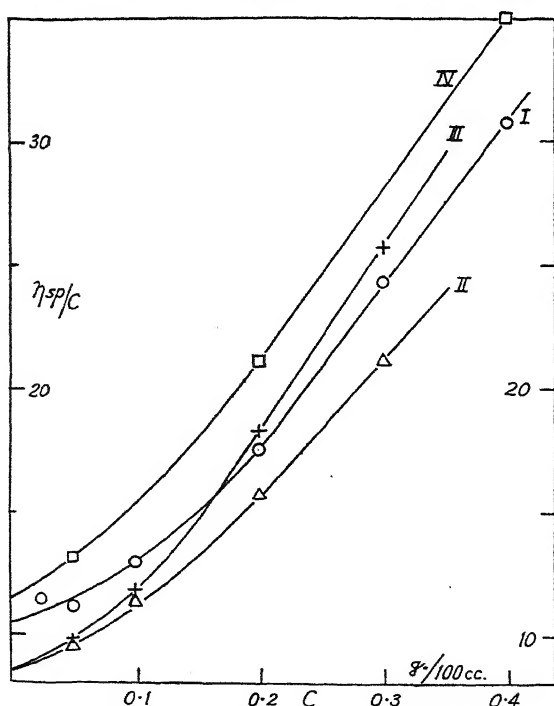


FIG. 1.—Viscosity of cellulose in four cuprammonium solvents.

It is also made clear that the Arrhenius equation $\frac{\log \eta_r}{c} = \text{const.}$ does not hold for the most dilute solutions, although Farrow and Neale⁸ and Duclaux and Dobry⁹ have shown that it is valid over higher concentration ranges.

Nor does the empirical equation of Fikentscher,¹⁰

$$(\log \eta_r)/c = \frac{75 k^2}{1 + 1.5 kc} + k,$$

which is even more successful as an expression of the variation of viscosity with concentration over the higher ranges, hold good at the very low concentrations tested in the present work. It predicts an increase of $(\log \eta_r)/c$ as c approaches zero, which is in general far less than that recorded.

The results show that for all four solvent compositions the value of η_{sp}/c rises with the concentration, slowly at first, and then more rapidly. Conversely $(\log \eta_r)/c$ falls rapidly at first and then more slowly. Moreover, the specific viscosity at any fixed cellulose concentration is by no means independent of the composition of the solvent, even when the cellulose concentration is very low. Reduction of the copper content first causes a fall and then a rise in specific viscosity, the rise being more marked at the higher concentrations of cellulose used. Decrease of ammonia content causes a substantial rise in the specific viscosity.

It is evident that for all four solvents the term η_{sp}/c used by Staudinger, varies both with the value of c and with the composition of the solvent. On the other hand, the term $\lim_{c \rightarrow 0} \eta_{sp}/c$ as used by Kraemer and Lansing, can be defined with a probable error of the order of 5 to 10 % provided that the composition of the solvent is specified.

TABLE III.—VALUES OF $\lim_{c \rightarrow 0} \eta_{sp}/c$.

CuAm I.	CuAm II.	CuAm III.	CuAm IV.
10.5	8.6	8.6	11.5

Cellulose in Phosphoric Acid.

Ekenstam¹¹ claims to have measured the molecular weight of celluloses from various sources in solutions of phosphoric acid. He is of the opinion that this reagent will not dissolve "native" cellulose, and confined his work to celluloses of relatively low viscosity derived mainly from Swedish filter paper. This was not borne out by a preliminary series of swelling experiments, however, in which we ascertained that there is an extremely critical concentration of solution (13.7 M, 81.5 %) having maximum solvent power on the cotton used in this investigation. Using such a solvent a 0.1 % solution of the cotton was prepared and its viscosity measured at 20° C. over a period of three days, using a shear-stress of 100 dynes/cm.². It was found that a homogeneous solution could not be obtained in less than five hours. The decrease of viscosity with time, due to the progressive hydrolysis of glucoside bridges and

⁸ Farrow and Neale, *J. Text. Inst.*, **T**, 1924, **15**, 157.

⁹ Duclaux and Dobry, *Comptes Rend.*, 1933, **197**, 1318.

¹⁰ Fikentscher, *Cellulosechemie*, 1932, **13**, 58.

¹¹ Ekenstam, *Ber.*, 1936, **69**, 549.

TABLE IV.—EFFECT OF TIME ON THE VISCOSITY OF CELLULOSE IN 13.7 M o-PHOSPHORIC ACID AT 20° C.

Time in hours after immersion of cellulose in acid	5	5½	6	6½	7	7½	8	12	24½	26½	72½	η of solvent
Apparent $\eta \times 100$	198	185	175	166	157	150	144	111	75.2	72.4	50.7	41.1

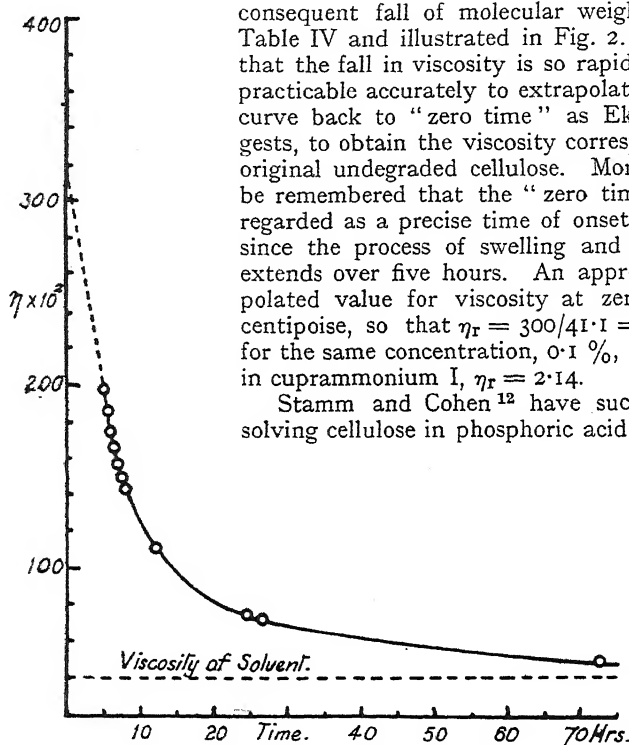


FIG. 2.—Cellulose in phosphoric acid.

value (113,000) for the molecular weight of cellulose than that deduced from the present data. Proof that the trituration of cellulose in acid does not accelerate breakdown appears to be lacking.

Cellulose Nitrate in Organic Solvents.

If it is supposed that cellulose can be converted into its nitrate without appreciable hydrolytic breakdown, the viscosity of solutions of the nitrate in organic solvents could then be used as a criterion of cellulose molecular weight.

Davidson's work¹³ suggests that little breakdown occurs during the nitration process, but that degradation occurs during denitration with ammonium hydrosulphide, so that the viscosity of the regenerated cellulose in cuprammonium is substantially less than the original.

¹² Stamm and Cohen, *J. Physic. Chem.*, 1938, 42, 921.

¹³ Davidson, *Shirley Inst. Mem.*, 1937-8, 16, 29.

Rigid proof of the common assumption that nitration can be effected without hydrolytic breakdown is therefore lacking. In spite of this, however, cellulose nitrates have been largely used for molecular weight estimation by physical methods, such as viscosity, osmotic pressure, and ultra centrifugal analysis, on account of their easy solubility.

Duclaux and Dobry⁹ have investigated the viscosities of solutions of nitrocellulose in various solvents and have concluded that at very low concentrations (of the order 0.04 %) the relative viscosity is independent of the solvent. This is taken as evidence that the solute is dispersed as single molecules, but apart from this the point is evidently of fundamental importance in the use of viscosity as a criterion of molecular chain length. In the present work it has been re-examined,

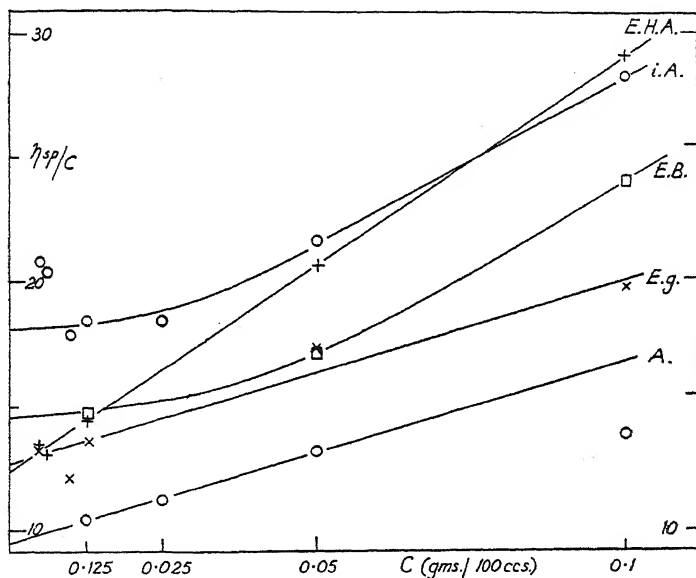


FIG. 3.—Viscosity of cellulose nitrate in various solvents.

A. = Acetone.
 E.g. = Ethylene glycol monoethyl ether.
 i.A. = iso-amyl acetate.
 E.B. = Ethyl benzoate.
 E.H.A. = 2-Ethyl hexyl acetate.

paying particular attention to the lowest concentrations, and to the relation between viscosity and concentration of solute. It will be seen that the conclusion of Duclaux and Dobry is not substantiated.

Nitration of the Cotton Cellulose.—The dried finely chopped cotton yarn was stirred for five hours in 150 times its weight of a mixture of two parts by volume of sulphuric acid (8.184) and one part by volume of nitric acid (8.142), maintained at 15° C. It was then washed first with glacial acetic acid, and then with distilled water till neutral. The product contained 12.0 % nitrogen, which corresponds to 2.3 NO₂ groups/C₆H₁₀O₅.

Viscosity of the Cellulose Nitrate.—The solvents chosen fell into two groups, the first, namely acetone, ethylene glycol monoethyl ether, and ethyl benzoate, differing in structural type, and the second, namely, iso-amyl acetate and 2-ethyl hexyl acetate differing in chain length.

TABLE V.—VISCOSITY OF CELLULOSE NITRATE IN ORGANIC SOLVENTS.*

A = Acetone, Eg = Ethylene glycol monoethyl ether iA = *iso*-amyl acetate, E.B. = Ethyl benzoate, E.H.A. = 2-Ethyl hexyl acetate.


Concn. gm./100 cc.	0.005.	0.00625.	0.01.	0.0125.	0.025.	0.05.	0.1.	0.2.	0.3.	0.4.	0.5.	0.6.
η_{sp} { A Eg iA E.B. E.H.A.}	—	—	—	0.13	0.28	0.66	1.39	4.19	9.9	21.4	41.4	73.9
	0.067	—	0.12	0.17	0.37	0.87	1.99	7.21	17.5	39.6	94.4	—
	0.104	0.127	0.178	0.23	0.46	1.08	2.83	11.2	31.8	79.9	190	—
	—	0.099	—	0.183	0.350	0.85	2.41	9.4	—	—	—	—
η_{sp}/c { A Eg iA E.B. E.H.A.}	0.067	0.081	—	0.186	0.419	1.03	2.91	13.7	—	—	—	—
	—	—	—	10.4	11.2	13.2	13.9	21.0	33.0	53.5	82.8	123
	13.4	—	12.0	13.6	14.8	17.4	19.9	36.1	58.4	99.0	189	—
	20.8	20.3	17.8	18.4	18.4	21.7	28.3	56.0	106	200	380	—
$(\log \eta)/c$ { A Eg iA E.B. E.H.A.}	—	15.8	—	14.6	17.1	17.1	24.1	47.2	—	—	—	—
	13.4	13.0	—	14.4	16.7	20.6	29.1	68.5	—	—	—	—
	—	—	—	4.26	4.29	4.40	3.78	3.58	3.46	3.37	3.25	3.12
	5.62	—	4.92	5.46	5.47	5.44	4.76	4.57	4.22	4.02	3.96	—
N { A Eg iA E.B. E.H.A.}	8.56	8.31	7.12	7.18	6.57	6.37	5.83	5.43	5.05	4.77	4.56	—
	—	6.56	—	5.83	5.21	5.35	5.33	5.09	—	—	—	—
	5.66	5.41	—	5.76	6.08	6.15	5.92	5.84	—	—	—	—
	—	—	—	1.00	1.01	1.02	1.10	1.06	1.11	1.11	1.17	1.21
N { A Eg iA E.B. E.H.A.}	1.00	—	1.01	1.01	1.00	1.01	1.05	1.22	1.20	1.24	1.43	—
	—	1.00	1.00	1.00	1.00	1.06	1.11	1.25	1.27	1.33	1.43	—
	—	1.00	—	1.00	1.00	1.04	1.10	1.23	—	—	—	—
	1.00	1.00	—	1.01	1.04	1.06	1.11	1.35	—	—	—	—

* All values except N refer to shearing stress (dynes/cm.²) = 31.6.

In each case an 0.5 % or 0.6 % solution was made up and filtered through a No. 3 Jena glass filter. The less concentrated solutions were prepared by successive dilution. The viscometers were filled with the taps free from grease, the taps then carefully greased, and the times of flow determined with the application of varying external pressures as already described. The kinetic energy correction was applied where necessary. It was usually of the order of 1 % of the observed time of flow, and even in the case of pure acetone at the highest shearing stress did not exceed 4 %.

The results obtained are given in Table V, and in Fig. 3 η_r/c is plotted for concentrations up to 0.2 %. On account of the smallness of the value of η_{sp} at low concentrations, the differences in the shapes of the curves as drawn in Fig. 3 cannot be regarded as significant. For example, for the 0.005 % solution in *iso*-amyl acetate, an error of 1 % in η leads to an error of 10 % in η_{sp}/c . It is therefore not possible to decide whether η_{sp}/c does or does not approach a constant value as c approaches zero. It seems clear, however, that the value $\lim_{c \rightarrow 0} \eta_{sp}/c$ varies quite definitely with the solvent, the relevant data being collected in Table VI.

TABLE VI.—SUMMARY OF CELLULOSE NITRATE IN ORGANIC SOLVENTS, AT 20° C.

Solvent.	Molecular Structure.	Mol. Wt.	η of Solvent $\times 10^2$ c.g.s.	Limiting Value of $\frac{\eta_{sp}}{c}$ as $c \rightarrow 0$.
Acetone . .	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} = \text{O} \\ \diagdown \\ \text{CH}_3 \end{array}$	58	0.312	9.5
Ethylene-glycol- monoethylether	$\begin{array}{c} \text{CH}_2 - \text{OH} \\ \\ \text{CH}_2 - \text{O} . \text{CH}_2\text{CH}_3 \end{array}$	90	2.09	13
2-Ethyl hexyl acetate . .	$\begin{array}{c} \text{CH}_3 - (\text{CH}_2)_3 - \text{CH} . \text{CH}_2 . \text{O} . \text{CO} . \text{CH}_3 \\ \\ \text{C}_2\text{H}_5 \end{array}$	172	1.51	13
Ethyl benzoate .	 $\text{CO} . \text{O} . \text{CH}_2 . \text{CH}_3$	134	2.18	14.5
<i>iso</i> -Amyl acetate	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} - (\text{CH}_2)_2 - \text{O} . \text{CO} . \text{CH}_3 \\ \diagdown \\ \text{CH}_3 \end{array}$	130	0.855	18

It is also evident from the data that both the quantity η_{sp}/c and the quantity $(\log \eta_r)/c$ vary so rapidly with c that their utility as a criterion of the molecular weight of the cellulose nitrate is seriously affected. Again, as with the case of the cuprammonium cellulose solutions, $\log \eta_r/c$ increases much more rapidly with c as $c \rightarrow 0$ than is predicted by Fikentscher's equation.¹⁰

Cellulose Acetate in Organic Solvents.

It was hoped that the cellulose could be converted into a suitable acetate whose viscosity in a number of solvents could be measured.

Despite the fact that several published methods were tried, however, it was not found possible to avoid extensive degradation during the acetylation process. The methods tried were those of Hess and Ljubitsch,¹⁴ which failed sufficiently to acetylate the cellulose used in the present work, and those of Irvine and Hirst,¹⁵ and Haworth and Machemer,¹⁶ both of which gave rise to degraded products.

The highest relative viscosity found for an 0.5 % solution in tetra chlorethane was 2.6 (compare cellulose nitrate in acetone, $\eta_r = 42.4$) and the lowest iodine number 0.63. The conclusion that acetylation of cellulose is accompanied by breakdown is confirmed by the recent work of Haworth and others,¹⁷ in which it is shown that where acetylation precedes methylation an "apparent molecular size" of 240 glucose units results, whereas with direct methylation in absence of oxygen the proportion of "end groups" appears to be zero.

Although Staudinger² admits that acetylation of cellulose is accompanied by degradation, in the course of his extensive researches on high polymers, he has made much use of the viscosity of cellulose acetates, without precise information as to the method of acetylation. Kraemer,¹⁸ in a recent paper, claims to have acetylated cellulose and regenerated it from the acetate without loss of viscosity, but details of the acetylation process are not given.

Viscosity and Degree of Polymerisation.

Probably the most reliable correlation between viscosity and degree of polymerisation is that afforded by the work of Kraemer and Lansing,³

TABLE VII.			D.P. = 260 $[\eta]$.
	$[\eta]$.		
Cellulose in CuAm I	10.5	2730	
" " " II	8.6	2230	
" " " III	8.6	2230	
" " " IV	11.5	2990	
	$[\eta]$.	D.P. = 270 $[\eta]$.	
Cellulose nitrate in acetone	11.5	3100	

in which ultra centrifugal analysis was used as a standard method, after it had been checked on polymers prepared from ω -hydroxy decanoic acid, whose molecular size is ascertainable by simple titration.

The use of their constants leads to the values for degree of polymerisation ($[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c$) shown in Table VII.

These values are close to the highest (3000) recorded by Kraemer³ for purified celluloses. They suggest that the nitration occurs without degradation, but this is not borne out by a comparison of the present data with those of Davidson,¹³ who nitrated with an anhydrous nitric acid-phosphoric acid mixture.

	Neale and Waite.			Davidson.
η cotton in CuAm 0.5 % soln.	.	.	0.26	0.18
η nitrate in acetone 0.1 % soln.	.	.	0.00745	0.0244

Although Davidson's sample of cotton had a lower cuprammonium viscosity, his nitrate showed a much higher viscosity than our own,

¹⁴ Hess and Ljubitsch, *Ber.*, 1928, 61, 1460.

¹⁵ Irvine and Hirst, *J.C.S.*, 1922, 121, 1585.

¹⁶ Haworth and Machemer, *ibid.*, 1932, 2270.

¹⁷ Haworth *et al.*, *ibid.*, 1939, 1885 and 1899.

¹⁸ Kraemer, *Ind. Eng. Chem.*, 1938, 30, 1200.

as would also be expected from the results of Berl and Rueff.¹⁹ It seems likely, therefore, that if Davidson's nitration procedure had been followed, we should have obtained a much higher D.P. for the nitrate than for the cellulose in cuprammonium. It would follow, if the Kraemer and Lansing constants are accepted, either that breakdown occurs in the cuprammonium solvent, in spite of the rigid exclusion of oxygen, or that association causing increase of chain length takes place in the phosphoric acid nitration process.

Summary.

A study has been made of the viscosities of dilute solutions of cellulose in cuprammonium solvents of varying copper and ammonia contents, and of solutions of the derived nitrate in various organic solvents.

All except the most dilute solutions showed anomalous flow, the apparent viscosity decreasing with the shearing stress applied.

Neither the logarithm of the viscosity nor the specific viscosity was found proportional to the concentration, and the value $\lim_{c \rightarrow 0} \eta_{sp}/c$ varied with the solvent. The degree of polymerisation of the sample used, deduced from the viscosity, indicated a molecule containing 2000-3000 glucose residues.

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¹⁹ Berl and Rueff, *Cellulosechem.*, 1933, 14, 115.

THE ETHANE-ETHYLENE-HYDROGEN EQUILIBRIUM.

BY E. A. GUGGENHEIM.

Received 5th March, 1941.

Since my article with the above title went to press, a note has appeared by Burcik, Eyster and Yost¹ commenting on the assignment of frequencies to ethylene made in 1939* by Conn and Sutherland.² This assignment is compared with Bonner's, which I had previously used, in the table. I have repeated my computations with the revised values for the frequencies, and I find that, so far as the modes $\delta (+ - +)$, $\delta (- - +)$, $\delta (+ + -)$ and $\delta (- + -)$ are concerned, none of the calculated values are affected. Any revision of the final results, therefore, depends entirely on the value assigned to the twisting mode $\delta (- - -)$.

Conn and Sutherland assigned to the twisting mode the value 700 cm^{-1} , which, as they point out, is too low to fit the experimental data on the heat capacity. However, Burcik, Eyster and Yost in their recent note claim that the spectroscopic data can be equally well interpreted

¹ Burcik, Eyster and Yost, *J. Chem. Physics*, 1941, 9, 118.

* I had unfortunately overlooked this paper owing to the fact that in its title only tetra-deutero-ethylene is mentioned, not ethylene.

² Conn and Sutherland, *Proc. Roy. Soc., A*, 1939, 172, 172.

TABLE I.—NORMAL MODES OF ETHYLENE.

Notation.†	Conn and Sutherland.		Bonner.	
	cm. ⁻¹	$\frac{\Theta_v}{100 \text{ deg.}}$	cm. ⁻¹	$\frac{\Theta_v}{100 \text{ deg.}}$
ν_0 (++++) .	1626	23.3	1623	23.3
ν_1 (++++) .	3020	43.2	3019	43.2
δ (++++) .	1343	19.2	1342	19.2
ν (---+) .	2988	42.8	2988	42.8
δ (---+) .	1444	20.7	1444	20.7
ν (+--+)	3107	44.5	3107	44.5
δ (+--+)	1020	14.6	950	13.6
ν (----)	3075	44.0	3069	44.0
δ (----)	1030	14.8	950	13.6
δ (+++)	950	13.6	940	13.5
δ (---)	943	13.5	1100	15.8
δ (---)	?	?	?	?

by assigning the value 829 cm.⁻¹. Not being in a position to judge the spectroscopic evidence, I have examined the effect on the thermodynamic quantities of using the value $\Theta_v = 1190^\circ$, corresponding to 829 cm.⁻¹, instead of the value $\Theta_v = 1290^\circ$, which I used previously.

Burcik, Eyster and Yost point out that the value $\Theta_v = 1190^\circ$ is in good agreement with all the experimental data on heat capacities, including three new measurements of their own. I still think that the value $\Theta_v = 1290^\circ$ gives, on the whole, slightly better agreement, unless one ignores the two measurements at 368° K. and 464° K. made by Eucken and Parts, but there is very little to choose between the two values.

As regards heat contents, I find that the lower value of Θ_v for the twisting mode leads to an increase of 0.02 in H/RT for ethylene at 355° K. and to an increase of 0.03 in the range 673° K. to 973° K. To obtain exact agreement between the calculated and experimental values of ΔH at 355° K., one now has to assume $-\Delta E_0/R10^3 = 15.51^\circ$ instead of 15.52°.

Using this value for ΔE_0 , and repeating the calculations of ΔG , I obtain results which throughout the range $T = 673^\circ \text{ K.}$ to $T = 973^\circ \text{ K.}$ can be accurately represented by the empirical interpolation formulæ:

$$\begin{aligned} \log_e \left(\frac{K_p}{\text{atm.}^{-1}} \right) &= -\frac{\Delta G^\dagger}{RT} = 15.51 \frac{10^3 \text{ deg.}}{T} - 16.23 \\ &\quad + 3.38 \log_e \left(\frac{10^3 \text{ deg.}}{T} \right) + 1.70 \left(\frac{T}{10^3 \text{ deg.}} \right), \\ -\frac{\Delta H}{R10^3 \text{ deg.}} &= 15.51 + 3.38 \frac{T}{10^3 \text{ deg.}} - 1.70 \left(\frac{T}{10^3 \text{ deg.}} \right)^2, \\ -\frac{\Delta C_p}{R} &= 3.38 - 3.40 \frac{T}{10^3 \text{ deg.}}. \end{aligned}$$

The effect on K_p is a decrease of 4 % on the previously calculated values throughout the range 673° K. to 973° K.

† This is the notation recommended by Conn and Sutherland.

Summary.

The calculations for the ethane-ethylene-hydrogen equilibrium recently published have been revised in view of a more recent assignment of the normal modes of ethylene. The result is a decrease of 4 % in the calculated values of K_p throughout the experimental temperature range 673° K. to 973° K.

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PERMEABILITY IN MONOLAYERS.

BY F. SEBBA * AND E. K. RIDEAL.

Received 19th March, 1941.

In some earlier publications¹ a new technique was described for examining how monomolecular films spread on water affected the rate of evaporation of the substrate, and the considerable reduction of the rate of evaporation shown by certain compressed films was discussed. In an attempt to throw further light on the mechanism of diffusion of the water through the monomolecular film, further experiments have been carried out but, instead of using simple films spread on water, complex films were used and the substrate, too, was varied in an attempt to find out how volatile substances dissolved in water evaporated through the film.

The apparatus was essentially the same in principle as the Evaporant described by Sebba and Briscoe,¹ and was designed in order that a comparison could be made of the quantity of water carried away by a constant stream of dry air with and without a film spread on the surface. The percentage ratio Q , which might be called the permeability ratio is 100 times the ratio between the quantity of water evaporated in a given time with a film spread on the surface compared to the quantity evaporated from a clean water surface under identical conditions of flow.

In the earlier paper, the preliminary hypothesis was advanced that it was not the physical state of the film itself which was decisive in determining the effect the film would have on the passage of water through it, but the proportion of water in the film itself.

In order to test this, the permeability ratio was measured for a film of egg albumin, spread on water of pH 7 beneath which tannic acid had been injected. This forms a complex film.² The tannic acid anchors itself under the protein making the film very much more rigid, so that although a protein film is easily dispersed by injecting saponin underneath, once "tanned" it remains stable. At 20 dynes/cm. surface pressure, which was the maximum pressure obtainable on the apparatus used, Q was found to be 100 % both for the simple albumin film, and

* 1851 Exhibition Scholar.

¹ J.C.S., 1940, 106.

² See Schulman and Rideal, *Proc. Roy. Soc., B*, 122, 29, 1937, in their papers on penetration.

the complex albumin-tannic acid film. The same results were obtained with gliadin-tannic acid films. This indicates again that the mechanical strength of the film is not a factor in determining Q .

Schulman and Rideal have shown that sodium cetyl sulphate when injected under a film of cetyl alcohol, penetrates in such a way that the cetyl sulphate orientates parallel to the cetyl alcohol. Under a film of cetyl alcohol, compressed to 9 dynes/cm., a solution of sodium cetyl sulphate was injected to bring its concentration in the substrate to 1 part in 500,000. The surface pressure of the cetyl alcohol complex film rose to about 45 dynes/cm. and at that pressure the permeability ratio was found to be 65 %, which is approximately of the same order as that of a film of cetyl alcohol compressed to the same pressure. Thus there is indirect confirmation of the hypothesis that the hydrocarbon end of the sodium cetyl sulphate penetrates between the cetyl alcohol chains.

The complex formed by injecting digitonin under a film of cholesterol, which itself has a Q value of 100 %, at a surface pressure of 40 dynes/cm. still had a Q value of 100 %.

Neutral phosphate when injected beneath a film of octadecylamine gives a very solid film. At a pressure of 24 dynes/cm., however, such

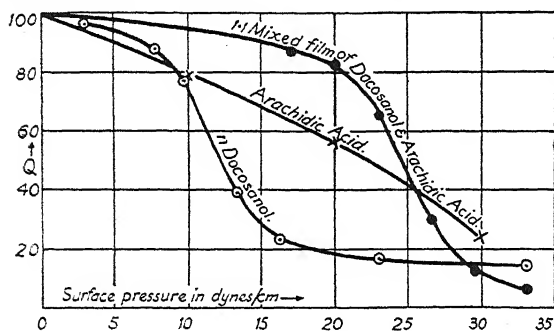


FIG. 1.
(References to arachidic acid on the figure are to eicosoic acid.)

a film still has a Q value of 100 %. At a surface pressure of 30 dynes/cm. octadecylamine itself, though it gives a solid film, has a permeability ratio of 100 %. This is in surprising contrast to octadecyl alcohol, which at that pressure has a Q ratio of 40 %.

Of the esters, a simple film of ethyl stearate compressed to 29 dynes/cm. was found to be considerably less permeable than stearic acid, giving a Q value of 30 %, compared to stearic acid which has a Q value of 82 % at the same surface pressure. Tripalmitin at 28 dynes/cm. has a Q value of 55 % whereas palmitic acid is completely permeable.

One example of a mixed film was investigated, a mixture of eicosoic acid and docosanol in the proportion of 1 to 1. The graph, Fig. 1, shows that the effect of mixing is to increase the Q value to more than the value for each of the components separately except at high pressures. This is surprising, as it would have been expected that with an acid and an alcohol, some closer association of the polar ends would have occurred improving the packing of the film, thus reducing Q .

An attempt has been made to investigate the effect produced by a monomolecular film spread on water on the volatilisation of volatile substances dissolved in the substrate. The choice of substances for

such an investigation is very limited, as the material has to be reasonably soluble in water and volatile from the solution, at room temperatures, and yet must not have sufficient affinity for the film-forming substance to render the film unstable. The two substances chosen were ammonia and ethyl alcohol.

A series of experiments were carried out using solutions up to 5 % by volume of ammonium hydroxide as substrate. The Evaporant was used as before with the exception that instead of collecting the water in a phosphorus pentoxide tube, the collected air was bubbled through 25 c.c. of a standard N./10 solution of sulphuric acid, and the excess sulphuric acid titrated with standard sodium hydroxide. As the concentration of ammonia was diminishing rapidly all the time due to volatilisation, the precaution was taken of starting with a fresh solution for each experiment and completing each stage of the experiment at a fixed time, *e.g.*, the cleaning of the surface was always done at exactly ten minutes after the solution was first put on the trough.

The technique otherwise was the same as before, the ratio between the quantity of ammonia evaporated in a given time with and without a film being determined. Unfortunately, the technique did not permit of sufficient accuracy for a complete curve of the variation of Q with surface pressure to be determined as in the case of pure water, and the film itself was not very stable, but the results obtained (Table I) seem to indicate that any monomolecular film has at least some retarding effect on the rate of volatilisation of ammonia from solution.

TABLE I.

Substrate.	Film.	Surface Pressure dynes/cm.	Vol. NaOH in c.c.	Q_{NH_3} , %.
3 % NH_3 Soln.	No film	0	10.5 ; 10.8	100
	Docosanols	3	9.8	92
		8	5.6	52
		12	4.2	39
		18	4.8	45
		28	0.8	7
	Stearic acid	26	8.4	78
	Eicosaic acid	30	0.6	6
	Octadecylamine	30 ; 30	8.9 ; 9.4	83 ; 88
5 % NH_3	No film	0	19.6 ; 21.1 ; 21.3 20.4 ; 22.7 ; 21.2 Av. = 21.1	100
	Docosanols	2.2	16.4	78
		6.4	10.5	50
		10.6	11.0	52
	Stearic acid	10	17.5	83
		15	16.5	78
		38	14.5	69
	Oleic acid	33	14.3	68
	Cholesterol	20	15.1 ; 18.0	72 ; 85
	Egg albumin	30	14.5	69
	Tanned octadecylamine			

Owing to the errors which may be due mainly to the existence of a diffusion gradient in the liquid, it is not considered that the Evaporant is the most suitable apparatus, but the results demonstrate that this marked screening effect of a film exists.

There appears also to be a specific screening effect for different types

of film as may be expected by analogy with the varying Q values for different films on pure water.

In order to throw further light on the subject, the volatilisation of ethyl alcohol through monomolecular films was investigated. This problem is doubly interesting. Firstly, as a short chain volatile polar compound, it should show an extreme form of the property of penetration and, secondly, would the superimposed film exert any preferential sieving effect on the volatilisation of the mixture of water and alcohol, in other words, was the concentration of alcohol entering the vapour phase the same with and without a film? In order to determine this, it became necessary to measure not only the quantity of water evaporated, but the quantity of alcohol, and the technical difficulties were not decreased by the rapid speed of the air current.

The apparatus, a modification of the original Evaporant circuit, was set up as in Fig. 2.

A, the first collecting tube of such a size to fit into a Dewar flask is cooled by liquid air and connected by a well-fitting ground glass joint to the Evaporant. No grease was used in the joint as the alcohol tends to dissolve it and carry it on to the measuring tube. In order to collect the fine snow which forms when the water is collected, and which may otherwise escape owing to the rapid current of air, the inside of the tube is packed with glass wool. A is connected to B, the tared measuring tube,

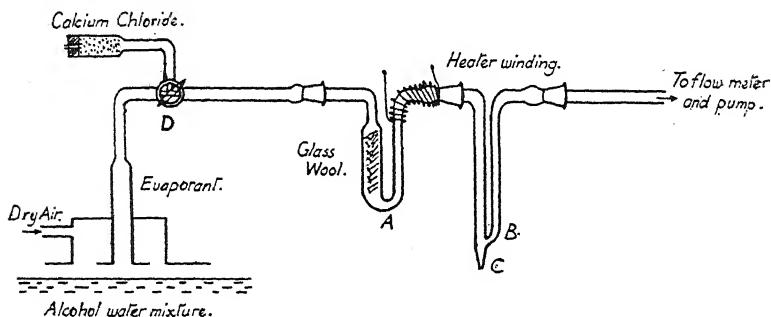


FIG. 2.

again by a greaseless ground glass joint, and the other end of B is connected by the usual greased ground glass joint to the flowmeter and suction apparatus. The tube B is simply a glass tube, bent into a U-tube with a thin capillary C drawn off at the bottom. Between A and the Evaporant, there is a three-way tap D, whose outlet to the air is via a fine capillary and a drying tube containing calcium chloride.

During a run, as soon as the collection of the alcohol-water mixture is required, the tap D is closed to the air, and a Dewar of liquid air is placed around A. The alcohol-water mixture is thus frozen out on to the glass wool. After a period of $7\frac{1}{2}$ minutes, tap D is closed to the Evaporant and opened to the air. Because of the capillary, a very slow current of dry air is now sucked through A to B. The Dewar is removed from A and placed around B, and after A has warmed up, a small flame is played all along A until all the alcohol-water mixture has been distilled into B. To prevent the mixture collecting in the joint between A and B, a heating coil is wound around it, and kept at a temperature of about 80°C . The flame is also played on the upper part of B, so that the liquid condenses on the lower portion of the tube near the point. B can now be removed, the joints stoppered, dried and weighed. The liquid drop is moved up and down the tube a few times to ensure homogeneity and then allowed to run into the capillary point C, which is broken above the prism of an Abbé refractometer, the drop run out and the refractive index determined.

Thus both the total weight of alcohol and water is obtained, and from the refractive index the proportions of the two.

The substrate, a 5 % alcohol solution was freshly placed in the trough before each experiment and the film spread after exactly ten minutes

TABLE II.

Method of Spreading.	Surf. Press in dynes/cm.	Total wt. Evaporated (g.).	Refractive Index.	% Alcohol.	Wt. Alcohol (g.).	Wt. Water (g.).	Q Alc. (%).	Q Wat. (%).
No film		0.1430 ; 0.1332 0.1398 ; 0.1344	1.3490 1.3485 1.3490 1.3481 1.3485 1.3494 1.3495	29	0.040	0.098	100	100
From old petrol ether solution	20 20 20 24	0.1154 0.1054 0.1284 0.1200	1.3460 1.3470 1.3468 1.3465	24.6 26.3 26.0 25.4	0.028 0.027 0.033 0.031	0.087 0.078 0.095 0.089	70 68 83 78	89 80 97 91
Similar but spread on water and alcohol injected beneath	36	0.1215	1.3464	25.2	0.031	0.091	78	93
Fresh benzene soln.	20 20 20 20	0.0298 0.0374 0.1212 0.0406	1.3420 1.3383 1.3482 1.3450	18.2 12.0 28.2 23.0	0.005 0.005 0.034 0.009	0.024 0.033 0.087 0.031	13 13 85 23	25 34 89 32
Similar but alcohol injected under film	37 42	0.1340 0.1138	1.3470 1.3482	26.2 28.2	0.035 0.032	0.099 0.082	88 80	100+ 84
Old benzene soln.	20	0.0768	1.3440	21.4	0.016	0.060	40	61
From benzene soln. to which drop of alcohol was added	20	0.1298	1.3470	26.2	0.033	0.097	83	99
Fresh petrol ether soln.	20 20	0.770 0.834	1.3440 1.3460	21.4 24.6	0.016 0.020	0.061 0.063	40 50	62 64
Similar but alcohol injected beneath film	36 37 37 42	0.0872 0.1074 0.0558 0.1379	1.3468 1.3520 1.3460 1.3685	26.0 34.4 24.6 28.6	0.023 0.037 0.014 0.040	0.064 0.070 0.042 0.098	58 93 35 100	65 71 43 100
Pentane soln.	20	0.0458	1.3415	17.2	0.008	0.038	20	39
From ethyl alcohol soln.	20	0.1200	1.3450	23.0	0.028	0.092	70	94

and a run done exactly ten minutes after that. Eicosoic acid was found to be a suitable substance for the film.

The results as tabulated in Table II are not as reproducible as could be desired, indicating a factor still obscure. The reasonable reproducibility of blank experiments on a clean surface of 5 % alcohol solution shows that there is no apparent fault in the technique. The most

interesting point which arises from these experiments is that the nature of the solvent in which the surface active substance is dissolved has some effect on the rate of evaporation, an effect which diminishes on continued passage of water and alcohol through the monolayer. That the solvent is retained for some time in the spreading film may be deduced from the fact that when a film of eicosoic acid is spread from benzene solution on a 5 % alcohol solution, it is very unstable at high pressures, the pressure falling rapidly resembling in this characteristic the behaviour of a liquid expanded film, although eicosoic acid spread directly on water gives a very rigid solid film at high pressures.

Though the number of experiments does not justify conclusions, it should be noted that a film of eicosoic acid spread from benzene slows the evaporation of the substrate and gives a distillate poorer in alcohol more readily than the same film spread from petrol ether.

The data suggest that in the course of time the effect of the "imprisoned" benzene on the permeability decreases, due to solution or evaporation. It appears that a film of eicosoic acid can considerably reduce the evaporation both of water and of alcohol from a 5 % solution; that the reduction is related to the way the film is spread on the surface, probably dependent on the solvent; there is some evidence also that the proportion of alcohol and water in the vapour differs from that in the solution, as well as from the proportion in the vapour when there is no film. If the last-mentioned difference is real, there is here an example of differential rates of permeability through a monomolecular film, which should have interesting analogies with biological behaviour.

Summary.

The permeabilities of a number of monolayers to water vapour have been examined in the Evaporant. Protein and tanned protein monolayers are freely permeable. The complex cetyl alcohol sodium cetyl sulphate film has a permeability similar to that of a cetyl alcohol monolayer. Ethyl stearate and the esters are very much less permeable than stearic acid. A mixed film of eicosoic acid and docosanol is more permeable than films of either component.

The evaporation of ammonia is retarded by monolayers and the retardations effected do not run parallel with the retardations of the passage of water vapour.

Monolayers retard the evaporation of a 5 % alcohol solution and differences due to the inclusion of the spreading fluid, especially benzene, in the monolayer are observed. The retardations in evaporation of alcohol and water from the solution do not appear to be identical, some evidence for selectivity being observed.

Our thanks are due to the Royal Commissioners for the Exhibition of 1851 for a Scholarship to one of us (F. S.), and to Professor H. V. A. Briscoe for the loan of an Evaporant.

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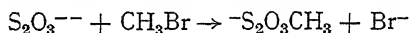
THE KINETICS OF THE REACTION BETWEEN METHYL BROMIDE AND THE THIOSULPHATE ION IN WATER.

By E. A. MOELWYN-HUGHES.

Received 21st October, 1940.

Among the very numerous reactions between ions and polar molecules in solution there are very few which do not have rates in agreement with the prediction of the classical collision theory.¹ The best known exceptions are the chemical changes involving an ion produced by the solvent, such, for example, as the saponification of esters, for which the anticipated rate exceeds the actual by a factor of about one thousand. There are, however, certain reactions between ions and polar molecules with rates slightly in excess of the theoretical values. We have undertaken the study of the present reaction in order to find out whether the difference is real, and if so, to seek its cause.

According to the results of Slator,² the following bimolecular reaction



proceeds without complications in water. Its absolute velocity, however, is about 17 times as great as we would expect it to be, if the collision theory is applied in its simplest form.

The procedure adopted resembles that described in earlier papers³ with modifications. To minimise the loss of the volatile reactant we first used reaction vessels constructed so as to make easy the formation of a stable film of dodecyl alcohol on the surface of the solution. With clean glass vessels, and using only the minimum pressure to express our reaction samples, we generally succeeded in finishing the run without breaking the film. Most of the experiments, the results of which are given here, were carried out in this way. Before the end of the work, however, we had in common use here a still more satisfactory device for excluding the vapour phase entirely. The apparatus shown in the figure is immersed in the thermostat, except for the capillary delivery tube, from which samples of the reaction mixture are expressed at requisite times into calibrated vessels containing known amounts of the chilling solution—in this case, standard iodine. Before the experiment is started, the whole apparatus is filled with clean mercury. The reaction

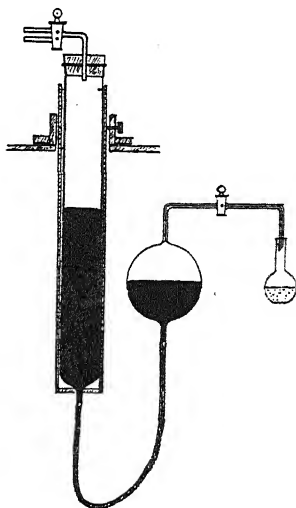


FIG. 1.

¹ Moelwyn-Hughes, *The Kinetics of Reactions in Solution*, Oxford University Press, 1933.

² *Trans. Chem. Soc.*, 1904, 85, 1286.

³ Moelwyn-Hughes, *Proc. Roy. Soc., A*, 1938, 164, 295; *Trans. Faraday Soc.*, 1939, 35, 368.

vessel may be filled by suction in less than a minute. The mercury reservoir is then raised, and clamped in a position giving a head of a few inches.

Because of a slight dilution effect, measurements have been made with solutions containing 49.7 millimols./litre of sodium thiosulphate, and 17.1 of methyl bromide.

Blank experiments showed the mercury to be inert. Thus, for example, 20 c.c. of the thiosulphate solution kept in glass for a week at 20° C. required 24.50 c.c. of standard iodine; the same volume kept over mercury for the same time required 24.46 c.c. In the most unfavourable circumstances the extent of reaction with mercury did not exceed 0.26 per cent. of the total change measured.

In order to be able to record an accurate initial time, the two reactant solutions must be violently mixed, which may account for a slight loss of organic halide before the reaction starts. Thus, for example, a stock solution of methyl bromide was found on analysis before and after a given set of runs to have the concentrations 32.5 and 31.9 millimols./litre. The concentration initially in solution was taken as one half of the mean of these two figures, *i.e.* as 16.1 ± 0.15 . After completion at 295.48° K in a solution containing initially 49.6 millimols./litre of thiosulphate, the extent of the total change was 13.8 millimols./litre. This would give us

$$K = \frac{[\text{Br}^-][-\text{S}_2\text{O}_3\text{CH}_3]}{[\text{CH}_3\text{Br}][-\text{S}_2\text{O}_3^-]} = 2.32.$$

In view, however, of the simultaneous hydrolysis of two of the molecules participating in this equilibrium, and of the difficulty mentioned above,

BIMOLECULAR VELOCITY CO-EFFICIENTS.

T.	$k \times 10^3$.	
	Observed.	Formula.
273.23	1.93	1.92
277.94	3.36	3.42
282.26	6.00	5.94
288.56	13.0	13.0
289.13	13.5	13.6
292.88	21.1	21.1
293.10	21.9	21.6
295.48	28.0	28.4
298.17	37.7	37.5

we have had to assume that the change goes to completion. The situation is thus not very satisfactory, but because we have examined it more thoroughly than the earlier workers did, we consider the results worthy of reproduction. They are given in summarised form in the Table where k represents the bimolecular velocity coefficient, expressed in litres per g. mol./sec. Those values for low temperatures are the more accurate, being correct to about 0.5 per cent. At the higher temperatures they are accurate only to 4.5 per cent. The figures in the last column are those reproduced by the empirical equation

$$k = 6.82 \times 10^{12} \times e^{-19,540/RT}.$$

From Slater's original work at three temperatures we obtain the values 5.05×10^{12} and 19,230 for the two numerical constants. The earlier work is thus fully substantiated.

On any reasonable estimate of the collision frequency, the first of these constants is too high by a factor of about 17. If, however, we allow for the fact that the electrostatic contribution to the energy of activation is a function of both the dielectric constant and the temperature and for the fact that at least one internal motion is called into action, then we may express the theoretical velocity coefficient as follows:

$$k = Z_0 \left(\frac{E_0}{RT} + 1 \right) e^{-E_0/RT} e^{-E_e/RT}$$

where

$$Z_0 = \frac{N_0}{1000} r_{AB}^2 \left\{ 8\pi kT \left(\frac{1}{m_A} + \frac{1}{m_B} \right) \right\}^{\frac{1}{2}}$$

N_0 and k are the constants of Avogadro and Boltzmann, m_A is the mass of the polar reactant, m_B that of the ionic reactant, and r_{AB} the distance apart of their centres when they react. The electrostatic contribution to the energy is

$$E_e = \frac{N_0 \mu_B z_A \epsilon}{Dr_{AB}^2}$$

where μ_B is the dipole moment of the molecule (1.80×10^{-18} e.s.u.), ϵ is the electronic charge (4.77×10^{-10} e.s.u.), z_B is the valency (-2) of the ion, and D (78.5) is the dielectric constant of the medium at the average temperature, T (285.7° K.). Using the notation and procedure of our previous papers, we then establish the identities

$$19,540 = E_0 - \frac{1}{2}RT - E_e(LT - 1)$$

$$\text{and} \quad 6.82 \times 10^{12} = Z_0 \left(\frac{E_0}{RT} + 1 \right) \exp \left\{ \frac{1}{2} - \frac{L\mu_B z_A \epsilon}{Dr_{AB}^2 k} \right\}$$

from which we evaluate r_{AB} by successive approximations. With $r_{AB} = 2.75 \times 10^{-8}$ cm., the right hand side of the latter equation becomes 7.28×10^{12} , in satisfactory agreement with experiment. E_0 becomes $19,540 + 285 - 135 = 19,690$ cal./gram-mole. For

$$L = - \left(\frac{\partial \ln D}{\partial T} \right)_P$$

we have used our previous figure of 4.63×10^{-3} .

We wish to thank Professor E. K. Rideal, F.R.S., and Dr. J. H. Shulman for giving us pure dodecyl alcohol and for showing us how to make stable films with it.

Summary.

The reaction between methyl bromide and the thiosulphate ion in water has been investigated experimentally as an interesting example of the very small number of reactions between ions and polar molecules which have rates slightly in excess of that given by the simple collision theory.

The participation of one internal mode of motion, and the contribution of a small electrostatic contribution to the activation energy, suffice to explain the apparent discrepancy.

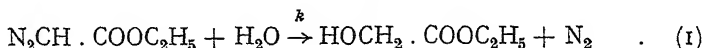
A simple apparatus is described which has been found satisfactory for examining reactions in solution where it is desirable to exclude the vapour phase.

THE KINETICS OF THE DECOMPOSITION OF DIAZOACETIC ESTER, CATALYSED BY ACIDS IN AQUEOUS SOLUTION.

BY E. A. MOELWYN-HUGHES AND P. JOHNSON.

Received 21st October, 1940, and as amended on 17th January, 1941.

The rate at which nitrogen is evolved from certain aqueous acidic solutions of diazoacetic ester obeys the unimolecular law

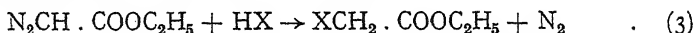


The unimolecular velocity coefficient, k , has been shown by Fraenkel¹ to be linearly related to the concentration, c_{H} , of hydrogen ion:

$$k = k_{\text{H}} c_{\text{H}} \quad (2)$$

Here k_{H} is the catalytic coefficient. It is regarded as such an accurately reproducible quantity that the reaction has not infrequently been used to determine the concentration of hydrogen ion in solution. The classical researches of Fraenkel, however, leave certain points in obscurity; and it is with a view to gaining a clearer insight into the mechanism of simple hydrogen catalysis that this work has been undertaken.

In the first place, a number of strong acids attack the ester molecule effecting substitution, according to the scheme



This behaviour is met with in the case of hydrochloric acid. On account of a partial removal of catalyst, the velocity of elimination of nitrogen

falls off at a greater rate than that given by the unimolecular law; and we have used this fact to estimate the extent of the substitution reaction.

In the second place, strong acids which do not appreciably attack the ester according to the substitution mechanism and which consequently give good unimolecular constants, yield catalytic coefficients which vary somewhat with the acid concentration. At 283.16° K,

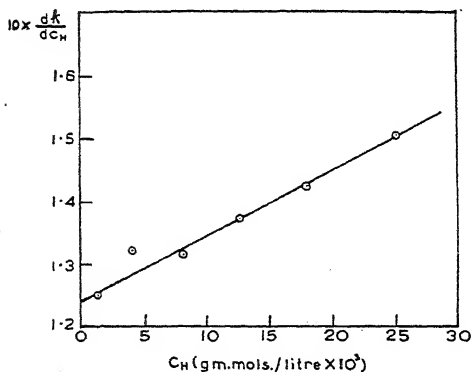


FIG. 1.

for example, using nitric acid, we find the unimolecular velocity constant to be given by the empirical relation

$$k = a + bc_{\text{H}} + dc_{\text{H}}^2 \quad (4)$$

¹ Fraenkel, *Z. physik. Chem.*, A, 1907, 60, 207.

where c_H is the concentration of hydrogen ion, in gram-mols./litre, and k is the unimolecular velocity coefficient, in reciprocal seconds. The specific constants b and d under these conditions have the values 0.124 and 0.525 (Fig. 1). The constant a , obtained by the difference between large quantities, cannot be assessed accurately, though it is not necessarily zero, as assumed by Brönsted and Bell for the corresponding reaction in benzene solution.²

Experimental.

Diazoacetic ester was prepared in the usual way³ by the action of sodium nitrite on a solution of glycine ester hydrochloride. Ether was removed from the ether extract at a temperature not exceeding 293° K by distillation *in vacuo*. Treatment with baryta was discarded in favour of repeated distillation *in vacuo*, the liquid coming over between 324.2° and 325.2° K at 17 mm. pressure being collected. Two different samples of the ester were so prepared, one of which was used at the temperature 273°, 283°, 293° K etc., and the other at intermediate temperatures. Analysis showed the ester to be $99.0 \pm 1\%$ pure. Solutions, usually about $M/20$, were prepared for each experiment by dissolving weighed amounts of ester in distilled water.

Stock acid solutions of approximately $N/10$ strength were prepared by diluting pure concentrated acids. A range of more dilute acid solutions was prepared by further dilution. Pipettes were washed successively with warm chromic acid, distilled water, and acetone and dried by a stream of air before every delivery of solution. The reaction vessel was similarly washed and dried by heating in a luminous flame and evacuating.

The acid concentration was calculated, assuming the density of the reaction mixture to be that of water at all temperatures. The "blank" vessel of the differential manometer⁴ used to measure the rate of the decomposition, contained acid solution of the same strength and volume as that in the reaction vessel. No correction for the solubility of nitrogen evolved in the reaction solution was necessary, since saturation of the solution occurs in the initial stages of the decomposition whilst the reaction mixture is attaining thermostat temperature. The experimental procedure after introducing solutions into the manometer vessels was the same as described previously.⁴ The unimolecular velocity coefficients were calculated from the expression

$$k = \frac{1}{t} \cdot \ln \frac{p_t}{p_t - p_i} \quad (5)$$

where p_t is the total pressure change, and p_i the pressure change at time t , by plotting $\log (p_t - p_i)$ against t .

Initial concentrations of ester were calculated from the total manometer deflection, the latter being calibrated to read volumes of gas evolved, for different temperatures and volumes of reaction mixture.

Influence of different Acids on the Decomposition of Diazoacetic Ester in Aqueous Solution.

Fraenkel¹ observed that the unimolecular velocity coefficients of the decomposition proceeding under the influence of hydrochloric and sulphuric acids showed a marked decrease with time. This was attributed to the removal of acid molecules by the reaction (3). In order to determine the extent of this side reaction, a detailed study of the effect

² Brönsted and Bell, *J.A.C.S.*, 1931, 53, 2478.

³ Gattermann's *Laboratory Methods of Organic Chemistry*.

⁴ Moelwyn-Hughes and Johnson, *T. Faraday. Soc.*, 1940, 36, 949.

in the decompositions catalysed by hydrochloric and nitric acids was undertaken.

The observations of Fraenkel on the diazoacetic ester decomposition

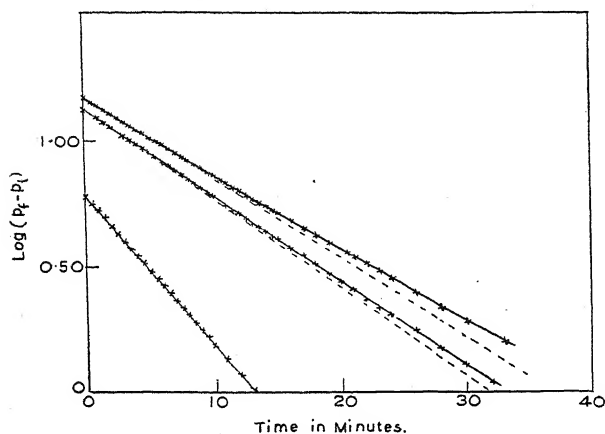


FIG. 2.—The decomposition of diazoacetic ester in the presence of HCl.

		$C_H \times 10^4$ gm.-mols./litre.	$C_E \times 10^3$ gm.-mols./litre.
Curve 1	.	36.59	8.14
„ 2	.	21.95	14.9
„ 3	.	21.97	30.6

in the presence of HCl were confirmed. If, however, the initial concentration of the ester was below 0.01 M a good unimolecular law was followed throughout the decomposition. For slightly higher initial concentrations of ester, the unimolecular constant decreased with time, but it was possible to obtain a good value for the initial stages of the decomposition. On plotting

k (if falling off occurs with time, the initial value is used) against c_H , a straight line apparently passing through the origin was obtained.

For concentrations of ester of about 0.03 M, a very considerable decrease in the unimolecular constant was observed during the course

TABLE I.—DECOMPOSITION OF DIAZOACETIC ESTER IN THE PRESENCE OF HCl AND HNO₃.

Concentrations in g.-mol./l.; velocity constants in reciprocal seconds.

Acid.	Temperature (°K).	$c_H \times 10^4$.	$c_E \times 10^3$.	$k(1) \times 10^4$.	$k(2) \times 10^4$.	$-(dc_E/dt) \times 10^4$.
HCl	298.12 ± 0.01	5.491	9.61	3.563	3.563	0
	298.11 ± 0.01	36.59	8.14	22.94	22.94	0
	298.11 ± 0.01	36.59	7.09	22.91	22.91	0
	298.12 ± 0.01	21.95	14.9	13.61	13.00	1.2
	298.10 ± 0.01	21.97	30.6	12.73	10.95	4.5
	298.10 ± 0.01	21.97	26.8	12.20	11.00	4.4
	298.12 ± 0.01	21.97	28.6	12.43	11.18	4.1
	298.11 ± 0.02	26.78	18.9	16.91	16.84	0.2
	298.11 ± 0.01	35.70	19.3	22.77	22.59	0.2
HNO ₃	298.11 ± 0.01	71.39	6.71	44.8	44.8	0
	298.11 ± 0.01	71.39	29.8	44.0	44.0	0
	298.11 ± 0.01	71.39	33.6	44.5	44.5	0

of the reaction. Since for these decompositions the initial values of k did not vary linearly with respect to c_H , it was assumed that the removal of acid by reaction (3) occurred rapidly during mixing of the solutions and attainment of thermostat temperature. The total decrease in acid concentration necessary to explain the decrease in k from the value in dilute ester solution to that for the final stages of the decomposition is given in Table I together with the initial concentrations of hydrogen ion, c_H , and of ester, c_E , and with $k(1)$ and $k(2)$, the velocity coefficients for the initial and final stages of the decomposition respectively (Fig. 2).

In contrast to these experiments, the decomposition catalysed by nitric acid follows a good unimolecular law, as shown in Table I. The initial concentration of ester has clearly no effect on the value of k .

Our results show that in the catalysis by nitric acid the amount of side reaction is undetectable. For this reason nitric acid was used as the catalyst in the experiments on the effect of temperature.

Table II demonstrates the reproducibility of

TABLE II.—REPRODUCIBILITY OF VELOCITY COEFFICIENTS.

Temperature (°K).	$c_H \times 10^3$.	$c_E \times 10^2$.	$k \times 10^4$.
298.11 ± 0.01	1.338	3.84	8.02
298.11 ± 0.01	1.343	2.80	8.04
298.11 ± 0.01	10.71	1.19	68.7
298.11 ± 0.01	10.71	1.49	69.0
293.39 ± 0.01	2.680	1.50	10.25
293.39 ± 0.01	2.680	3.26	10.23
283.16 ± 0.02	21.47	2.49	29.14
283.16 ± 0.03	21.47	1.60	29.02

TABLE III.

$t(\text{sec.})$	$(p_f - p_i)_{\text{obs.}}$	$(p_f - p_i)_{\text{calc.}}$
$(T = 273.29 \pm 0.03 \text{ } ^\circ\text{K. } k_{\text{obs.}} = 4.509 \times 10^{-4} \text{ sec.}^{-1})$		
360	11.72	11.70
420	11.41	11.40
480	11.09	11.09
540	10.79	10.79
600	10.51	10.51
660	10.25	10.23
720	9.99	9.95
780	9.70	9.69
840	9.42	9.43
900	9.19	9.18
960	8.94	8.93
1020	8.69	8.69
1080	8.45	8.46
1140	8.22	8.24
1200	8.00	8.02
1260	7.79	7.80
1320	7.56	7.60
1380	7.39	7.39
1440	7.20	7.22
1560	6.81	6.82
1680	6.49	6.46
1800	6.11	6.12
1920	5.79	5.79
2040	5.49	5.49
2160	5.20	5.20
2280	4.91	4.93
2400	4.68	4.67
2580	4.30	4.30
2760	3.96	3.97
2970	3.60	3.61
3180	3.29	3.28
3420	2.96	2.95
3600	2.72	2.72
3900	2.40	2.37
4230	2.05	2.05
4560	1.80	1.76
4800	1.60	1.58
5100	1.41	1.38
5400	1.26	1.21
$(T = 303.13 \pm 0.03 \text{ } ^\circ\text{K. } k_{\text{obs.}} = 5.464 \times 10^{-3} \text{ sec.}^{-1})$		
15	8.03	8.06
30	7.43	7.43
45	6.83	6.84
60	6.28	6.31
75	5.78	5.81
90	5.33	5.35

TABLE III.—*Continued.*

$t(\text{sec.})$	$(p_f - p_t)_{\text{obs.}}$	$(p_f - p_t)_{\text{calc.}}$
$(T = 303.13 \pm 0.03^\circ \text{K. } k_{\text{obs.}} = 5.464 \times 10^{-3} \text{ sec.}^{-1})$		
105	4.91	4.93
120	4.51	4.54
135	4.17	4.19
150	3.85	3.86
165	3.53	3.55
180	3.26	3.27
195	3.00	3.02
210	2.80	2.78
225	2.56	2.56
240	2.38	2.36
255	2.21	2.17
270	2.02	2.00
285	1.87	1.85
300	1.71	1.70
315	1.55	1.57
330	1.46	1.44
345	1.32	1.33
360	1.22	1.23
390	1.03	1.04
$(T = 328.16 \pm 0.03^\circ \text{K. } k_{\text{obs.}} = 2.009 \times 10^{-3} \text{ sec.}^{-1})$		
15	9.20	9.13
30	8.90	8.86
45	8.60	8.60
60	8.38	8.34
75	8.05	8.09
90	7.87	7.85
105	7.62	7.62
120	7.38	7.39
135	7.14	7.17
150	6.95	6.96
165	6.74	6.76
180	6.50	6.55
195	6.35	6.36
210	6.17	6.17
225	6.00	5.99
240	5.74	5.81
255	5.62	5.64
270	5.47	5.47
285	5.30	5.31
300	5.17	5.15
315	5.00	5.00
330	4.86	4.85
345	4.70	4.71
360	4.58	4.57
375	4.46	4.43
390	4.28	4.30
405	4.18	4.17
420	4.08	4.05
450	3.85	3.81
480	3.59	3.59
510	3.40	3.38
540	3.17	3.18
570	2.99	3.00
600	2.82	2.82
630	2.68	2.66
660	2.49	2.50
690	2.37	2.36
720	2.20	2.22
780	1.97	1.97
840	1.73	1.74
900	1.58	1.55
960	1.39	1.37
1020	1.25	1.21

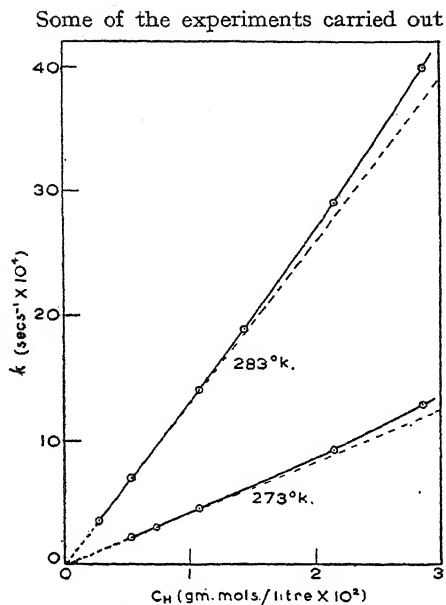
bility of our results. Table III, containing values of $(p_f - p_t)$ observed and calculated from equation (5), illustrates the accuracy of fast and slow experiments for the whole temperature range covered.

The Influence of Temperature on the Decomposition of Diazoacetic Ester in the presence of Nitric Acid.

First order velocity coefficients for a range of concentrations of nitric acid were determined at intervals of 5° between the temperatures 273° and 318° , and at 328° and 338° K; k was plotted against c_H for each temperature. This plot, covering usually a ten-fold change in acid concentration, proved, for all temperatures between 288° and 313° K (inclusive), to be a straight line represented by equation (4) with $d = 0$. The constants of the equation, for each temperature, were derived by the method of least squares. Deviations from the linear behaviour were met at 273° and 283° K, when the acid concentrations exceeded 0.015 N (Fig. 3).

TABLE IV.—UNIMOLECULAR VELOCITY COEFFICIENTS.

Temperature (°K).	$c_H \times 10^4$.	$c_E \times 10^3$.	$k \times 10^4$.	
			Obs.	Calc.
273·22 ± 0·02	53·67	3·76	2·190	2·194
273·23 ± 0·01	71·61	1·56	2·982	2·969
273·29 ± 0·03	107·4	3·09	4·509	4·519
273·31 ± 0·02	214·8	1·90	9·168	9·166
273·29 ± 0·03	286·5	1·31	12·78	12·27
278·11 ± 0·04	17·90	3·94	1·296	1·311
278·11 ± 0·04	35·80	3·24	2·641	2·71
278·11 ± 0·04	107·4	1·67	8·45	8·31
278·11 ± 0·04	214·9	0·95	16·65	16·71
283·16 ± 0·03	26·85	3·22	3·351	3·359
283·16 ± 0·03	53·69	2·72	6·907	6·902
283·17 ± 0·03	107·4	2·24	13·98	13·99
283·16 ± 0·05	143·2	0·92	18·90	18·71
283·16 ± 0·03	214·7	1·60, 2·49	29·08	28·15
283·16 ± 0·03	286·5	1·38	39·88	37·64
288·00 ± 0·01	13·46	3·62	2·619	2·675
288·00 ± 0·01	26·83	3·62	5·837	5·785
288·00 ± 0·01	53·65	2·96	11·99	12·00
288·00 ± 0·02	107·3	1·28	24·41	24·43
293·39 ± 0·01	13·45	4·19	4·796	4·92
293·39 ± 0·01	26·80	1·50, 3·26	10·24	10·11
293·39 ± 0·01	53·60	3·10	20·57	20·54
293·39 ± 0·01	107·2	1·90	41·37	41·41
298·11 ± 0·01	13·40	3·84, 2·80	8·03	8·19
298·11 ± 0·01	26·78	1·89	16·9	16·87
298·11 ± 0·01	53·70	1·93	22·7	22·66
298·11 ± 0·01	53·56	1·16	34·4	34·25
298·11 ± 0·01	71·39	0·671, 2·98, 3·36	44·4	45·82
298·11 ± 0·01	107·1	1·49, 1·19	68·9	68·99
303·13 ± 0·03	5·350	3·48	3·625	3·784
303·13 ± 0·04	13·42	2·78	12·43	12·32
303·13 ± 0·04	26·75	2·23	26·51	26·42
303·13 ± 0·04	53·50	1·76	54·64	54·74
308·33 ± 0·03	2·671	4·94	2·293	2·33
308·33 ± 0·03	5·342	4·36	6·705	6·77
308·33 ± 0·03	7·118	2·17	9·835	9·72
308·33 ± 0·03	26·69	2·04	42·23	42·25
313·20 ± 0·04	2·665	3·02	3·785	3·323
313·20 ± 0·04	5·325	2·72	10·23	10·36
313·18 ± 0·05	13·36	1·92	30·74	31·63
313·20 ± 0·04	17·76	1·27	43·76	43·28
313·20 ± 0·04	26·65	1·91	66·92	66·80
318·16 ± 0·03	0·6645	2·00	1·06	—
318·16 ± 0·02	1·329	2·60	2·178	—
318·18 ± 0·01	2·659	3·86	5·748	—
318·18 ± 0·01	5·318	3·11	15·04	—
318·18 ± 0·03	7·092	1·61	23·20	—
318·16 ± 0·03	8·888	1·68	31·38	—
328·19 ± 0·02	0·6612	2·27	3·275	—
328·16 ± 0·04	1·323	1·53	5·879	—
328·16 ± 0·03	2·645	2·32	14·23	—
328·16 ± 0·03	3·529	1·17	20·09	—
328·20 ± 0·03	5·290	2·27	33·44	—
328·19 ± 0·03	7·057	1·07	49·95	—
338·35 ± 0·04	2·634	1·69	26·65	—
338·23 ± 0·05	5·267	0·78	66·80	—



The first order velocity coefficients for each temperature are contained in Table IV alongside initial acid and ester concentrations. Values of k_H , the bimolecular velocity coefficient of the reaction, are given in Table V. Concentrations are given in g.-mol./litre, k in sec^{-1} , and k_H in sec^{-1} litres/g.-mol.

The constants of the following equation:

$$\ln k_H = \bar{C} + J/R \cdot \ln T - E/RT \quad (6)$$

were determined by the second of the two methods described in our previous work.⁴

We find:

$$\ln k_H = 44.6801 - 4.615 \cdot \ln T - 18890/RT \quad (7)$$

The best fit to an equation of the Arrhenius type is:

$$\ln k_H = 29.0968 - 17500/RT \quad (8)$$

Comparison of the sum of the squares of the percentage deviations of k_H calculated from (6) and (7) with k_H observed, shows that the Arrhenius equation gives a slightly better agreement with experimental results. We thus conclude that J is either zero or has a small negative value. Table V contains, in addition to observed values of k_H , those calculated according to equation (8). $\Sigma \epsilon^2$, the sum of the squares of the percentage deviations of these calculated values from those observed, is given at the

TABLE V.—THE INFLUENCE OF TEMPERATURE ON THE VELOCITY COEFFICIENTS.

Temperature (°K).	$k_H \times 10^2$.	
	Obs.	Calc.
273.27 ± 0.05	4.328	4.355
278.21 ± 0.04	7.816	7.718
283.16 ± 0.03	13.20	13.42
288.00 ± 0.01	23.17	22.64
293.39 ± 0.01	38.92	39.71
298.11 ± 0.01	64.89	63.87
303.13 ± 0.03	105.8	104.2
308.33 ± 0.03	166.2	170.0
313.20 ± 0.04	264.7	265.2
318.17 ± 0.04	(455.9)	411.8
		$\Sigma \epsilon^2 = 23.6$

foot of the table. The catalytic coefficient may be expressed as follows:—

$$k_H = 4.27 \times 10^{12} \times e^{-17500/RT} \quad (8)$$

The reaction thus closely resembles that studied in the foregoing paper, and a similar explanation of the fairly fast rate may be accepted.

Summary.

The kinetics of the decomposition of diazoacetic ester in aqueous solution under the influence of various strong acids has been studied experimentally over as wide a range of conditions as possible. The work confirms and extends the researches of Fraenkel.

THE KINETICS OF THE MUTAROTATION OF GLUCOSE, CATALYSED BY HYDROGEN ION IN AQUEOUS SOLUTION.

By P. JOHNSON AND E. A. MOELWYN-HUGHES.

Received 21st October, 1940.

In pure water and in aqueous solutions of various catalysts, glucose mutarotates according to the unimolecular law:

$$k = \frac{1}{t} \ln \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty} \quad (1)$$

where α_t is the rotation at time t , and α_0 and α_∞ are the initial and final rotations. When the solution contains moderate concentrations of strong acid, the unimolecular velocity constant, k , is the sum of two terms, namely:

$$k = k_0 + k_H c_H \quad (2)$$

where k_0 is the velocity coefficient of the uncatalysed reaction in the pure solvent, k_H is the catalytic coefficient, and c_H is the concentration of hydrogen ions. We have carried out this investigation in order to find out whether the two apparent energies of activation

$$RT^2 \frac{\partial \ln k_0}{\partial T} \quad \text{and} \quad RT^2 \frac{\partial \ln k_H}{\partial T}$$

are equal, as Hudson and Dale first supposed them to be.¹

We have carried out a series of mutarotations with pure α -glucose at four temperatures, keeping the ionic strength constant at each one by adding the requisite amount of potassium chloride to the hydrochloric acid which was used as a catalyst. The constants k_0 and k_H have been determined by the method of least squares, except in one case, where only three concentrations of acid were used, and they were evaluated graphically. Our results for k_0 agree excellently with those independently determined in pure water by Kendrew and Moelwyn-Hughes² whose method and apparatus we have used in the present work.

¹ *J. Amer. Chem. Soc.*, 1917, 39, 320.

² *Proc. Roy. Soc., A*, 1940, 176, 352.

From four series of experiments conducted at ten degree intervals of temperature, it is found that, at 298.15°K ,

$$RT^2 \frac{\partial \ln k_H}{\partial T} = 18,980 \text{ cal.} \quad (3)$$

A more representative value is obtained by examining the independent results of other investigators. The most accurate value for the apparent energy of activation of the uncatalysed reaction in pure water at the same temperature is

$$RT^2 \frac{\partial \ln k_0}{\partial T} = 16,945 \text{ cal.} \quad (4)$$

The difference between the two energies is a real one. The anomaly of a fast, catalysed reaction having an energy of activation greater than the corresponding slow, uncatalysed reaction is apparent only, for it

TABLE I.

$T(^{\circ}\text{K})$.	$c_G \times 10$.	$c_H \times 10^3$.	$k \times 10^4$.	
			Observed.	Calculated.
282.98 ± 0.02	3.11	20.11	1.309	1.305
282.97 ± 0.01	2.99	40.22	1.718	1.723
282.99 ± 0.01	3.30	50.28	1.934	1.932
293.21 ± 0.02	3.91	20.05	3.841	3.817
293.11 ± 0.01	2.68	40.25	5.090	5.185
293.11 ± 0.01	3.16	60.20	6.616	6.536
293.11 ± 0.01	3.55	80.26	7.854	7.895
303.16 ± 0.01	2.50	7.90	7.905	7.95
303.14 ± 0.01	3.31	20.03	10.36	10.31
303.14 ± 0.02	3.75	40.06	14.32	14.22
303.14 ± 0.02	3.78	50.07	16.10	16.17
313.38 ± 0.02	2.98	1.968	16.73	16.68
313.38 ± 0.01	3.35	3.936	17.72	17.76
313.30 ± 0.01	3.32	7.86	19.81	19.93
313.38 ± 0.01	3.15	9.84	21.30	21.02

has been shown that the true energy of activation for the uncatalysed reaction is 22,915 cal. We may infer, though we have not proved, that the temperature variation of the term in equation (3) is less than that of the term in equation (4).

Experimental Details.

The specimen of α -glucose was the same as in the previous work, showing an initial specific rotation of $[\alpha]_{5893 \text{ \AA}}^{293^\circ \text{K}} = 110.0^\circ$. 2-3 grams were taken from the vacuum desiccator, and made up to 50 c.c. of solution, using stock HCl solutions containing 0.1004 gram-equivalents per litre. The pipette deliveries were checked by weighing. Reaction vessels were washed with chromic acid, distilled water and alcohol, and dried in a stream of hot air. The water was of the same purity as in our previous work. The use of the new double jacketed polarimeter tube (4 dm.) enabled the temperature to be maintained at a value constant to $\pm 0.02^\circ$, and occasionally to within $\pm 0.01^\circ$.

Experimental Results.

Because the accuracy of the present experiments is comparable with that attained in the study of the uncatalysed reaction, no detailed data for individual runs are given. The results in summarised form appear in Table I, where c_G and c_H denote, respectively, the concentration of glucose and hydrogen ion in gram-equivalents per litre. The unit of the uni-molecular velocity coefficient, k , is the reciprocal second. Calculated values cited in Table I are those reproduced by equation 2, using the observed constants, k_0 and k_H , which are given in Table II.

TABLE II.

T (°K.).	$k_0 \times 10^6$.		$k_H \times 10^3$.	
	J. and M.-H. Analytical Extrapolation from Catalytic Experiments.	K. and M.-H. Direct observation from noncatalytic Experiments.	Observed.	Calculated (equation 5).
282.98 ± 0.02	8.87	8.63	2.08	2.08
293.11 ± 0.01	24.6	24.7	6.77	6.70
303.14 ± 0.02	64.1	64.3	19.5	19.7
313.38 ± 0.01	156	159	55.2	55.1

The values of k_0 derived by means of equation 2 agree satisfactorily with those determined by Kendrew and Moelwyn-Hughes² for the mutarotation in pure water. The figures under k_H calculated in Table II are those given by an equation of the Arrhenius type, with $E_A = 18,980$ cal. The individual values of $RT^2 \frac{\partial \ln k_H}{\partial T}$ are 19,190, 18,610, and 19,190 cal., which suggest a minimum in the neighbourhood of 298.1° K, much as in the case of ionisation

heats in water.³ The figure 18,980 is intermediate between that of 19,300 found by Kilpatrick and Kilpatrick,⁴ and of 18,030 found by Moelwyn-Hughes,⁵ though nearer the former. A value of about 19,000 cal. would thus appear to be the energy of activation of the catalysed reaction. A comparison of the various data, however, shows that the velocities afforded by the dilatometric method employed by the American workers are higher than those afforded by the polarimetric method, which is the more accurate one. Table III, where the comparison is made, contains also some figure due to Hudson and Dale.¹ An analysis of these combined results leads us to the conclusion that in

TABLE III.

T (°K.).	$k_H \times 10^3$.		Investigator.
	Observed.	Calculated.	
273.10	0.62	0.64	K. and K.
282.10	2.02	2.08	M.-H.
282.98	2.08	2.12	J. and M.-H.
287.90	3.83	3.69	M.-H.
293.10	7.02	6.72	K. and K.
293.11	6.77	6.72	J. and M.-H.
293.38	6.76	6.87	M.-H.
298.10	10.0	11.1	H. and D.
298.10	12.8	11.1	K. and K.
298.30	11.4	11.4	M.-H.
303.10	17.3	18.9	H. and D.
303.14	19.5	19.0	J. and M.-H.
303.34	19.1	19.4	M.-H.
313.38	55.2	52.3	J. and M.-H.

³ Harned and Owen, *Chem. Rev.*, 1939, 25, 31.⁴ *J. Amer. Chem. Soc.*, 1931, 53, 3698.⁵ *Z. physikal. Chem., B*, 1934, 26, 272.

the temperature interval 283°-303° K, the apparent energy of activation of the catalysed reaction is $18,560 \pm 180$ cal. The calculated values of Table III are those given by the equation

$$\log_{10} k_H = 11.657 - 18,560/2.303RT. \quad (5)$$

Both k_0 and k_H are composite velocity coefficients. In order to convert the observed catalytic coefficient to the essentially bimolecular constant governing the interaction of α -glucose and hydrogen ion, we have the relation

$$k_2 = k_H \left(\frac{K}{K+1} \right) \quad (6)$$

where K is the equilibrium constant 0.575, which has been shown by Kendrew and Moelwyn-Hughes¹ to be virtually independent of temperature. It follows that

$$k_2 = 1.656 \times 10^{11} \times e^{-18560/RT}. \quad (7)$$

Discussion.

Let us assume that the catalytic mutarotation of glucose by hydrogen ion in water is a simple bimolecular change, governed by those collisions where the energy in a specified direction exceeds a critical value, E . Then

$$k_2 = Z_0 \left(1 + \frac{E}{RT} \right) e^{-E/RT}. \quad (8)$$

Taking Z_0 , the standard collision frequency, to be proportional to $T^{\frac{1}{2}}$, it follows that E is 18,850 cal. at 293.25°. Consequently, Z is 8.19×10^9 , litres per g.-mol./sec., or 1.35×10^{-11} c.c. per mol./sec. The latter quantity should be comparable with the theoretical standard collision frequency

$$Z_0 = S \left(\frac{kT}{2\pi m} \right)^{\frac{1}{2}}$$

where S is the target area on the heavy molecule (here glucose) and m is the mass of the light molecule (here the hydrogen ion). Doubt exists as to whether we should treat the hydrogen ion in water as a permanently solvated structure, with, say, six molecules of water attached to it, or as an elementary ion. On the first supposition S becomes 22.63×10^{-16} cm.²; on the latter 2.17×10^{-16} cm.². In view of the absence of specificity in the hydrogen catalysed mutarotation of sugars, we incline to favour the second supposition.

Summary.

The mutarotation of glucose under the influence of hydrogen ions in water has been investigated experimentally. The results show that the apparent energy of activation of the catalysed reaction exceeds that of the uncatalysed reaction at the same temperature by some 2000 cal. The anomaly is probably only apparent; the real energy of activation of the uncatalysed reaction exceeds the apparent value for the catalysed reaction. The molecular statistics of the catalysed mutarotation suggest that it is the naked, rather than the solvent-sheathed, hydrogen ion that is effective.

We are indebted to the Chemical Society for assisting us to buy some of the chemicals used in these three investigations. One of us wishes also to record his indebtedness to the Department of Scientific and Industrial Research for a maintenance allowance.

*The University Chemical Laboratory,
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10. OCT 1941

SYSTEMATICS OF BAND-SPECTRAL CONSTANTS. PART VI.* INTERRELATION OF EQUILIBRIUM BOND CONSTANT AND INTERNUCLEAR DISTANCE.

BY C. H. DOUGLAS CLARK AND K. R. WEBB.

Received 21st December, 1940.

1. Introduction.

In Part IV various relations connecting equilibrium vibration frequency and separation of diatomic nuclei, as suggested by different authors, were compared. It appeared that the modification of Morse's formula suggested by Clark reproduced the experimental data rather better than the other proposals. The relation has also been applied with some success to linkages in compounds,¹ and further investigations on these lines are in progress.

At the same time it appears that neither the original Morse expression nor our modification has the dynamically correct form, because the harmonic relation between frequency and bond constant requires the inclusion of the reduced mass of the two atoms concerned in a linkage when frequency and separation are interrelated. For this reason the Morse-Clark formula does not meet the case of isotopic forms, where the frequencies are different but the separations closely alike, and Allen and Longair's proposal² was made. Essentially all other suggestions have involved the interrelation of bond constant with linkage separation, and Sutherland^{3,4} has stressed that the relation should take this form. We shall return to this objection after presentation of our results.

Clark and Stoves⁵ have observed that the error introduced when applying the Morse-Clark expression to the isotopic di-atoms ^{10}BO and ^{11}BO is within the experimental error. In the case of hydrogen, hydrides and deuterides,⁶ where the error would be large, introduction into the expression of an isotopic factor meets the experimental requirements quite well. This change is essentially equivalent to interrelating bond constant with separation in accordance with dynamical requirements.

* Parts I, II, III in these *Transactions*, 1937, **35**, 1390; Part IV, 1938, **34**, 1324; Part V, 1940, **36**, 370.

¹ Thompson and Linnett, *J. Chem. Soc.*, 1937, 1884 *et seq.*

² Allen and Longair, *Phil. Mag.*, 1935 (vii), **19**, 1032.

³ Sutherland, *Proc. Ind. Acad. Sci.*, 1938, **8**, 341; *J. Chem. Physics*, 1940, **8**, 161.

⁴ Sutherland, *Ann. Rep. Chem. Soc.*, 1938, 46.

⁵ Clark and Stoves, *Nature*, 1935, **136**, 682.

⁶ Clark and Stoves, *Phil. Mag.*, 1939 (vii), **27**, 389.

⁷ Clark, *Nature*, 1939, **143**, 800.

⁸ *Ibid.*, **144**, 285.

In these circumstances, it seems well worth while to examine whether bond constant and internuclear distance can be related in such a way as to retain the advantages of the Morse-Clark expression. Some progress has already been made.^{7, 8} This development is expanded in the following section.

2. New Relations Between Bond Constant and Internuclear Distance.

The following three lines of argument lead to relations of similar form between bond constant k_e and internuclear distance r_e :—

(1) Carbon-Carbon Linkages. In Part V, arising from the discussion of the interrelation of dissociation energy with internuclear distance, Clark derived equation (5) of that communication, a relation which may be written in the form

$$k_e r_e^{5n\frac{1}{2}} = k_{qr} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is the Group Number of the link, and k_{qr} a sub-period constant, sensitive to configurational type ($qr = ss, sp, sd$ or pp).

The Morse-Clark relation, corresponding to equation (2) below, has always given relatively large errors for CC. Whilst no explanation can be given at present of the fact that these links require a special expression, it is clear that for a given r_e and k_{qr} (1) gives larger k_e than equation (3) below, which may correspond to the relatively great stability of CC linkages, and to the particular form of their potential energy—nuclear distance curve.⁹

(2) Linkages of Similar Reduced Mass.—Starting from the Morse-Clark relation $\omega_e r_e^{3n\frac{1}{2}} = k_{qr}$, and combining it with the harmonic expression $k_e = 4\pi^2 c^2 \omega_e^2 \mu$, where μ is the reduced mass of the two atoms concerned, eliminating ω_e , we have $k_e r_e^{6n}/\mu$ constant, so that for linkages of similar μ we may expect a relation of the form

$$k_e r_e^{6n} = k_{qr} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which is that also suggested by Sutherland.⁴

Hydrides of a given period have μ closely alike, so here we may expect (2) to apply. Clark and Stoves⁶ used $\omega_e r_e^{3n\frac{1}{2}} = i k_{qr}$, where i is an isotopic factor equal to $\sqrt{\mu(\text{HH})/\mu}$, giving $\omega_e r_e^{3n\frac{1}{2}} \mu^{\frac{1}{2}} = \text{constant}$, for hydrides, of the same form as (2).

(3) Linkages in General.—Dr. J. J. Fox pointed out to us in a private communication that for symmetrical di-atoms (XX type) of the KK period μ increases with n so that very approximately $\mu \propto n^{\frac{1}{2}}$. It may be shown that the rule includes the non-symmetrical cases. We find further that it holds best within a given sub-period: thus in KK ss , $n^{\frac{1}{2}}/\mu$ for LiLi equals 0.25; in KK sp , values for BeO and BeF are equal, 0.30; in KK pp , for seven di-atoms from CC to OO, the values lie in the range 0.26 to 0.29. With this assumption, the Morse-Clark relation yields

$$k_e r_e^{6n\frac{1}{2}} = k_{qr} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The constancy of the expression $\omega_e r_e \mu^{\frac{1}{2}} n^{\frac{1}{2}}$, of the same form as (3), was discovered empirically in the KK period by Webb.

If the values of Sutherland's product p in Part V are used, it is found that in a given sub-period $p r_e$ is approximately constant: thus

⁹ Fox and Martin, *J. Chem. Soc.*, 1939, 884.

for KKss, *sp* and *pp* the function has mean values 26.4, 28.3 and 27.0 respectively. If we multiply this by $Dr_e^3 n^{\frac{1}{2}} = \text{constant}$ (see Part V), and use Sutherland's relation $k_e r_e^2 = pD$, where D is dissociation energy, we again obtain (3). This argument refers only to ground states.

3. Comparison with Experiment.

We first test (1) for CC links. The k_{qr} values are such that for given r_e , k_e is larger for linkages in compounds than for the di-atom CC, which may be associated with relatively greater firmness of binding in the case of the compounds. It is fortunate in simplifying the relations that for CC the value of $4\pi^2 c^2 \mu n^{\frac{1}{2}}$ is approximately unity ($\mu = 6 \times 1.65 \times 10^{-24} = 9.90 \times 10^{-24}$ gram, $c = 3 \times 10^{10}$ cm. per sec., $n = 8$). It follows from $k_e = 4\pi^2 c^2 \omega_e^2 \mu$ that $k_e n^{\frac{1}{2}} = \omega_e^2$, so that we may write for CC links in organic compounds

$$\left. \begin{aligned} k_e r_e^5 n^{\frac{1}{2}} &= \omega_e^2 r_e^5 = 1.14 \times 10^7 \\ k_e r_e^5 &= 4.03 \times 10^6 \end{aligned} \right\} \quad (4)$$

and for the di-atom CC in ground and excited states

$$\left. \begin{aligned} k_e r_e^5 n^{\frac{1}{2}} &= \omega_e^2 r_e^5 = 1.02 \times 10^7 \\ k_e r_e^5 &= 3.60 \times 10^6 \end{aligned} \right\} \quad (5)$$

where ω_e is in cm.^{-1} , r_e in Å, and k_e in dynes per cm.

Fox and Martin⁹ have found that relations of the type (4) give excellent agreement with experiment. Table I shows that equation (5) gives good concordance in the case of the di-atom CC.

TABLE I.

Electronic Levels of Di-atom CC.	k_e dyne/cm. $\times 10^{-5}$.	r_e (expt.) Å.	r_e (calc.) Å.
d $^1\Pi_g$	11.79	1.251	1.250
B $^3\Pi_g$	11.29	1.261	1.262
b $^1\Pi_u$	9.08	1.315	1.317
A $^3\Pi_u$	9.47	1.308	1.307

If we take $k_e r_e^5 n^{\frac{1}{2}}$ and $k_e r_e^6 n^{\frac{1}{2}}$ equal to 10^7 and 1.22×10^7 respectively, the mean KKpp constants, the errors are somewhat greater than those in Table I by the former, and become considerable by the latter formula: moreover, the errors are all negative. The argument, therefore, supports the use of equations (4) and (5) in the ways suggested.

Table II summarises a considerable amount of calculation of mean percentage errors in deriving r_e from k_e by equations (1), (2) and (3) for non-hydride di-atoms and for hydrides of the KH period. The k_e 's are first calculated from ω_e 's by means of $k_e = 3.55 \times 10^{22} \omega_e^2 \mu$ (ω_e cm.^{-1} , $\mu = 1.649 \times 10^{-24} M_1 M_2 / (M_1 + M_2)$ gram, where M_1, M_2 are the two atomic weights (O = 16), so that k_e is in dynes per cm. Using r_e in Å, the values of the functions of equations (1), (2) and (3) are calculated, the averages for a given sub-period being taken as k_{qr} : thus, for the KKss sub-period, by Table II, $k_{qr} = 1.43 \times 10^7$ for equation (3). The r_e 's are next calculated using these sub-period constants, and the mean percentage difference errors found, as in the last three columns of the table. The means for 79 levels are as shown at the foot, whence

it appears that (1) gives generally worse results than (2) and (3), which are about equally satisfactory.

In constructing Table II, the data for one excited state of BO ($B^3\Sigma^+$) have been omitted, since these and other formulæ fail to reproduce the experimental figures, which are therefore presumed to be in error. Further, although the number of cases for KK $\dot{p}p$ is given as 20, the k_{qr} 's are those originally calculated for 24 states which include CC. It has not been thought worth while to recalculate results for this period entirely without CC, as very little difference is made to the mean errors in r_e . The case of CC is omitted in calculating the mean errors for this sub-period.

It is noteworthy that (a) the k_{qr} 's rise steadily from the KK to the KM periods, falling again at LL, suggesting that k_{qr} has a periodic

TABLE II.

Period.	Sub-Period.	Number of Levels.	Ranges.		$k_{qr} \times 10^{-7}$.			Mean Per Cent. Diff. Errors in r_e (calc.).			
			n.	$\mu (\times 10^{24})$ gram.	Equation.						
					(1).	(2).	(3).				
								$k_e r_e^5 n^{\frac{1}{2}}$.	$k_e r_e^6 n$.	$k_e r_e^6 n^{\frac{1}{2}}$.	
Equation.								(1).	(2).	(3).	
KH	{	$s\sigma$	2	0	0	0.107	0.287	0.203	8.19	2.70	2.70
		$p\sigma$	2	0	0	0.168	0.388	0.224	0.08	0.12	0.12
		$p\pi$	4	1	0.02	0.167	0.438	0.163	1.06	0.61	0.57
		ss	3	0	0	0.492	2.03	1.43	1.21	1.80	1.80
KK	{	sp	5	1	0.5.	0.818	3.27	1.13	0.73	0.37	0.67
		$\dot{p}p$	20	4	2.4	0.998	3.82	1.22	1.56	0.96	0.76
KK ⁺	{	$\dot{p}p$	7	2	1.8	0.913	3.29	1.06	2.77	1.22	1.23
KL		$\dot{p}p$	16	3	1.0	1.91	9.40	3.00	2.63	1.79	1.80
KM		sp	2	0	0	2.42	14.3	4.77	0.25	0.31	0.31
	$p\dot{a}$	2	0	0	2.32	12.1	3.83	1.51	0.88	0.88	
LL	{	ss	3	0	0	0.733	3.53	2.49	2.35	2.94	2.94
		$\dot{p}p$	6	4	3.2	3.31	23.3	6.74	4.14	2.14	2.13
<u>MM</u>	{	ss	2	0	0	1.25	7.16	5.06	0.41	0.30	0.30
<u>MM</u>		$\dot{p}p$	2	0	0	4.41	39.8	10.6	5.98	3.69	3.69
<u>NN</u>		$\dot{p}p$	3	2	0.5	9.90	101	28.0	7.90	5.95	6.60
Mean Percentage Difference Errors (79 cases)									2.44	1.54	1.53

character; (b) the divergence in k_{qr} for sub-periods of a given period is least in the KK period and increases to LL, and probably afterwards in higher periods; (c) the k_{qr} 's of di-atom ions are less than those for corresponding neutral di-atoms, thus $k_{qr}(\text{KK}^+) < k_{qr}(\text{KK})$, as in the case of the Morse-Clark formula.

The fact that equations (2) and (3) give errors closely alike is to be expected. Where the experimental data in a given sub-period contain only cases for which the group numbers n are the same, the method used in assigning k_{qr} 's will ensure identical errors by the two formulæ: this occurs in every line where the range of $n = 0$. In other cases, differences may arise by the two formulæ, but these are never large. This seems to be due to the ranges of μ in any sub-period being always small: the largest in the table is 3.2×10^{-24} gram. Equation (2) was devised

to meet the case of similar reduced masses, and if (3) is a more general form, we shall expect the observed resemblances.

The fact that the function $k_e r_e^6 n'' = k_{qr}$ gave about equally good results for $\gamma = \frac{1}{2}$ or 1 led us to examine which value of γ actually gave the best constancy in the KK $\rho\rho$ sub-period, where data on 20 levels are available. The error curve is relatively flat in the region $\gamma = 0.2$ to 1.0, after which it rises steadily. The best value of γ in this sub-period is 0.62, which tends to support equation (3) rather than (2).

Where the Morse-Clark expression gives good results, the di-atoms concerned, including their isotopic forms, in each sub-period show no large variations in μ . The nature of k_{qr} is unknown: it may happen that it contains a factor which is a function of the average μ of the sub-period concerned. The argument advanced by Sutherland against the expression^{3, 4} thus loses much of its weight.⁹

The calculations amongst hydrides are incomplete, only those in the KH period being reported upon. Further work now in progress on other hydrides yields similar results, and will be communicated fully elsewhere.

It appears that formulæ of the present type may find extended usefulness in application to linkages occurring in compounds, as in the case of the carbon-carbon linkages discussed by Fox and Martin.

4. Comparison Between Different Formulæ.

Table III shows different functions which have been equated to constants for linkages of similar types by different authors. The method of Huggins^{10, 11} (see Part IV) is not capable of representation in this way.

TABLE III.

Authors.	Function involving k_e and r_e .	Corresponding Function involving ω_e and r_e .
Morse . . .	$k_e r_e^6 \mu^{-1}$	$\omega_e r_e^3$
Morse-Clark . . .	$k_e r_e^6 n \mu^{-1}$	$\omega_e r_e^3 n^{\frac{1}{2}}$
Badger . . .	$k_e (r_e - d_{ij})^3$	$\omega_e^2 (r_e - d_{ij})^3 \mu$
Allen-Longair . . .	$k_e r_e^6$	$\omega_e r_e \mu^{\frac{1}{2}}$
Fox, Clark (CC) . . .	$k_e r_e^5$	$\omega_e^2 r_e^5$
Clark, Sutherland . . .	$k_e r_e^6 n$	$\omega_e r_e^3 n^{\frac{1}{2}} \mu^{\frac{1}{2}}$
Clark, Webb . . .	$k_e r_e^6 n^{\frac{1}{2}}$	$\omega_e r_e^3 n^{\frac{1}{2}} \mu^{\frac{1}{2}}$

Apart from exponents, Badger's function is the only one containing an adjustable constant (d_{ij}). Sutherland³ suggested a modification of this, $k_e r_e^3 n^{\frac{1}{2}}$ or $\omega_e^2 r_e^3 n^{\frac{1}{2}} \mu$. This does not work

well; for example, the values of $k_e r_e^3 n^{\frac{1}{2}}$ for 3 electronic states of NO are 4.41, 9.73 and 7.94 in the same units, the corresponding r_e 's being 1.41, 1.06 and 1.15 respectively. It is noteworthy that the function changes in the opposite sense to r_e , and this is found for other di-atoms. This suggests a modified Badger function of the form

$$k_e (r_e - d_{ij})^3 n^{\frac{1}{2}} = C_{ij}. \quad (6)$$

That this expression has possibilities is seen as follows. If we combine two states of OO where the r_e 's are least and greatest, we get $d_{ij} = 0.64$; using this, the function (6) is 0.703 and 0.711 for the ground states of CN and OO respectively. On the other hand, the value is 0.297 in the

¹⁰ Huggins, *J. Chem. Physics*, 1935, 3, 473.

¹¹ *Ibid.*, 1936, 4, 308.

same units for the ground state of LiLi: possibly better concordance with experiment might be obtained if allowance were made for configurations. We have not pursued this further on account of the success of our power formulæ.

We may summarise the errors calculated by different formulæ for hydride⁶ and non-hydride (Part IV) di-atoms. Numbers of levels involved are placed in brackets.

TABLE IV.

	Badger.	Allen-Longair.	Huggins.	Morse-Clark.	Here.
Hydrides .	5.04(44)	5.46(44)	3.18(44)	1.40(41)	0.99(8)
Non-hydrides .	3.46(70)	2.77(70)	2.12(68)	1.80(70)	1.55(71)
Totals .	4.08(114)	3.80(114)	2.54(112)	1.65(111)	1.46(79)

It appears that the accuracy of the Morse-Clark expression is maintained. The Badger and Allen-Longair expressions, which take no account of electron configurations, give the largest errors. Huggins' method, which allows for configurations, occupies an intermediate position, but is extremely tedious in application.

Sutherland,³ referring to the original Morse expression, states that this rule held best for molecules in which the masses of the atoms were approximately equal. Clark,¹² however, showed that the function gave errors of the order of 25 per cent. for the symmetrical di-atom LiLi, and that in ground states it possessed a periodic character.¹³ The success of the formula in certain cases seemed to be due to the fact that those used came near where the periodic curve crossed the zero error line. It was to correct the observed periodicity that the group number was introduced. Morse restricted the use of his expression to similar cases, so that our extension to di-atoms of similar configuration follows in a natural manner.

Summary.

Relations of the form $k_e r_e^{-x} n^y = k_{gr}$, where k_e is equilibrium bond constant and r_e nuclear distance, n group number, and k_{gr} a sub-period constant, have been examined. It is found that with $x = 6$, $y = \frac{1}{2}$ or 1 good reproduction of present data is obtained, and the most suitable values of k_{gr} have been assigned. It seems probable that a value of y in the region $\frac{1}{2}$ to $\frac{2}{3}$ may ultimately be found most satisfactory. In the case of the di-atom CC, the empirical data require $x = 5$. The results obtained compare favourably with those arising from suggestions made by other authors.

Discussion due to Drs. Fox and Martin, Linnett, Newing and Sutherland during the preparation of this paper and the following Part VII is gratefully acknowledged.

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¹² D. Clark, *Phil. Mag.*, 1934, (7), 18, 459.

¹³ Clark, *Physic. Rev.*, 1934 (ii), 47, 238.

SYSTEMATICS OF BAND-SPECTRAL CONSTANTS. PART VII. THE EMPIRICAL FORM OF RELATIONS INVOLVING GROUP NUMBER.

By C. H. DOUGLAS CLARK.

Certain independent lines of argument tend to support the form of relation between bond constant and distance examined in Part VI.

Sutherland,¹ starting with a potential function of the form $U = ar^{-M} - br^{-N}$, has derived the relations

$$k_e r_e^{M+2} = aM(M - N) \quad (1)$$

$$p = MN = k_e r_e / D \quad (2)$$

where D is dissociation energy. Further, Linnett² has recently examined a potential function of the type $U = ar^{-M} - be^{-Nr}$, whence it follows that

$$k_e r_e^{M+2} = a[M(M - 1) - p'r_e] \quad (3)$$

where p' is the MN of Linnett's function. Putting $M = 4$ in (1) and (3),

$$k_e r_e^6 = a(16 - p) \quad (4)$$

and

$$k_e r_e^6 = a(20 - p'r_e) \quad (5)$$

respectively, which are of the empirical power form. In order to argue further, we must consider the possible variations of a , p and $p'r_e$ for

TABLE I.

Group No. <i>n</i>	2	8	9			10		11	12	
Sub-group	<i>s</i>	<i>c</i>	<i>b</i>	<i>a</i>		<i>b</i>	<i>s</i>	<i>a</i>	<i>s</i>	
<i>a</i> × 10 ⁻⁵ {	KK period.	LiLi	CC	BeF	BO	CN	CO	NN	NO	OO
		5.6	8.4	4.8	5.5	7.5	7.0	7.6	6.6	6.4
	KK ⁺ period				CO ⁺	NN ⁺			OO ⁺	
					6.6	8.6			6.1	
Di-atom type .	<i>ss</i>	<i>pp</i>	<i>sp</i>	<i>pp</i>	<i>pp</i>	<i>pp</i>	<i>pp</i>	<i>pp</i>	<i>pp</i>	

di-atoms of similar electron configuration. We restrict ourselves to the KK and KK+ periods, where the experimental data are most abundant.

(a) Variation of a .—Linnett assumes $M = 3$, and finds a variation of a in the KK period, so that a different value must be taken for each individual di-atom. The results appear somewhat obscured by the fact that the cases are not arranged in the order suggested by the periodic classification. When this plan³ is taken into account, Linnett's values of a show considerable regularity (Table I).

Linnett attempted to account for larger a 's in terms of smaller nuclear charges ($a(\text{NO}) > a(\text{OO}^+)$) and larger number of electrons

¹ Sutherland, *Proc. Ind. Acad. Sci.*, 1938, 8, 341.

² Linnett, *Trans. Faraday Soc.*, 1940, 36, 1123.

³ Clark, *ibid.*, 1935, 31, 1017.

($a(\text{CO}) > a(\text{CO}^+)$). But there are also considerable variations amongst "orthosteres" (equal numbers electrons and total nuclear charge): thus $a(\text{NN}) > a(\text{CO})$; $a(\text{CN}) > a(\text{BO}) > a(\text{BeF})$; $a(\text{NN}^+) > a(\text{CO}^+)$. A third factor must be taken into account, namely, symmetry of distribution of charge. The a 's tend to fall with increasing asymmetry of nuclear charge. Linnett omitted BeO (8c), but we may expect $a(\text{BeO}) < a(\text{CC}) = 8.4$. The effect of electron configuration on a is also clearly seen in Table I.

If we now consider, with Linnett, the di-atoms of the $\text{KK}pp$ class which are formed from the atoms C, N and O, we have the following descending series of a values with increasing n :

$$\text{CC} > \text{CN} > \text{NN} > \text{CO} > \text{NO} > \text{OO}.$$

This suggests that a bears some inverse relation to n . It seems probable that the variation in sub-groups of a given group noticed above is hardly as great as would appear from Table I: thus $a(\text{NN}^+)$ is possibly too high, and should be nearer $a(\text{CO}^+)$. Linnett suggests $a(\text{NN}^+) = 7.2$. Further, neglecting the uncertain D of the CO ground state, $a(\text{CO}) = 7.3$ which is near $a(\text{NN})$. We have examined different functions ($an^{\frac{1}{2}}$, $an^{\frac{2}{3}}$, an) for comparison (Table II), using Linnett's

TABLE II.

Di-atom	CC	CN	NN	CO	NO	OO
Group No. n	8	9	10	10	11	12
$a (\times 10^{-8})$	8.4	7.5	7.6	7.0	6.6	6.4
$an^{\frac{1}{2}} (\times 10^{-8})$	2.38	2.25	2.40	2.21	2.19	2.22
$an^{\frac{2}{3}} (\times 10^{-8})$	3.36	3.30	3.53	3.25	3.26	3.36
$an (\times 10^{-8})$	6.72	6.75	7.60	7.00	7.26	7.68

assignments of a . It appears that $an^{\frac{1}{2}}$ and $an^{\frac{2}{3}}$ approach constancy, whilst an tends to increase with n .

(b) **Variation of p .**—Sutherland³ found p closely alike for related di-atoms. Clark (Part V) has shown p as a periodic function, varying in the KK period from 9.9 to 23.4 for LiLi and NN respectively, reaching a maximum value in Group 10. The variation in a given sub-period, however, is not very large: thus in $\text{KK}pp$ extreme values are 20.7 (CC) and 23.4 (NN).

(c) **Variation of $p'r_e$.**—It has been shown empirically (Part VI, end section 2) that in a given sub-period $p'r_e$ is approximately constant, hence we may perhaps reasonably expect that $p'r_e$ will not vary very greatly amongst related di-atoms. For constant M_1 we shall expect Nr_e constant. Using Linnett's calculated values of N , we find the following mean values of Nr_e : CC 2.58, CN 2.46, CO 2.54, NN 2.54, NO 2.43, OO 2.59.

Sutherland deduced Allen and Longair's relation from (4), but this involves constancy of a and p in a given sub-period, a condition which does not appear satisfactory. It is now recognised that these magnitudes may vary amongst related di-atoms, and even for different states of the same di-atom. We thus find it difficult to interpret the results in terms of the form of potential function used by Sutherland.

When we consider Linnett's results, assuming from Table II constancy of $an^{\frac{1}{2}}$ in the $\text{KK}pp$ sub-period, and k_{qr} proportional to $20 \cdot p'r_e$,

we find the form $k_e r_e^6 n^{\frac{1}{2}}$ is suggested by equation (5). Table II shows imperfect constancy of an , confirming our opinion that the above is a rather more general form than $k_e r_e^6 n$. With reference to the constancy of $an^{\frac{1}{2}}$ in Table II, it is perhaps worthy of note that the empirical investigation previously noted (Part VI, end section 3) led to the best exponent of $n = 0.62$ in the $KKpp$ sub-period.

Further consideration shows, however, that Linnett's work does not reproduce the empirical data as well as at first appeared. Equation (5) is based upon $M = 4$, whereas Linnett took $M = 3$. Hence $k_e r_e^x n^{\frac{1}{2}}$ with $x = 5$ is supported rather than with $x = 6$. In the $KKpp$ sub-period, the mean percentage error in calculating r_e using $x = 5$ is 1.56 (Part VI, Table II), whilst Linnett obtained 1.5. Yet both our and Linnett's work shows that better reproduction of the experimental data is obtained (except for CC links) using a $k_e r_e^6$ type ($M = 4$) formula rather than $k_e r_e^5$ ($M = 3$).

We have therefore examined the effect of putting $M = 4$ in Linnett's equations. The resulting mean values of a for the six cases of Table II are ($\times 10^{-5}$): CC 6.3, CN 4.8, CO 5.3, NN 5.5, NO 3.9, OO 4.2. It becomes clear that the general regularities previously noted for $M = 3$ no longer appear. We find that Linnett's work, whilst it reproduces the empirical form $k_e r_e^x n^y$ and supports the introduction of the group number n , is more consistent with $x = 5$ than with $x = 6$. Linnett's potential function appears inadequate to this extent. Too much reliance, however, should not be placed upon results obtained in one sub-period only.

We refer, in conclusion, to some independent work of Newing.⁴ Using a molecular model in which n valency electrons are considered as an electron gas occupying volume V , he finds⁵ that in the neighbourhood $r = r_e$ the electronic kinetic energy T can be written in the form

$$T = kn^{\frac{2}{3}} V^{-\frac{2}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where k is constant. Assuming with Newing that V increases with nuclear separation r in such a way that $V = (cr)^m$, where c is a function of n and the nature of the nuclear cores and independent of r , it follows that

$$T = kn^{\frac{2}{3}} (cr)^{-2m/3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6a)$$

Further, Slater⁶ has shown, by an application of the virial theorem, neglecting zero-point vibrational energy, that

$$T = -U - r \frac{dU}{dr} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and that $\frac{dT}{dr}$ might be interpreted as the repulsive force near $r = r_e$.

In this case, (6a) appears to imply a repulsion exponent $2m/3$ in the potential energy function. If we equate this to $M = 4$ previously found, we have $m = 6$. Further, since when $r = r_e$, the first and second differential coefficients of U with respect to r are zero and k_e respectively, (7) gives

$$\left(\frac{dT}{dr}\right)_{r=r_e} = -k_e r_e \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

From (6a), we get $\left(\frac{dT}{dr}\right)_{r=r_e} = -\frac{2kmn^{\frac{2}{3}}}{3c^{2m/3}r_e^{(2m+3)/3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$

whence, equating the right hand sides of (8) and (9),

$$3k_e r_e^{(2m+6)/3} c^{2m/3} = 2kmn^{5/3} \quad (10)$$

Inserting $m \times 6$ as found above, we have

$$k_e r_e^6 c^4 = 4kn^{5/3} \quad (10a)$$

which is evidently of our empirical form. It would be identical with $k_e r_e^6 n^{5/3} = k_{qr}$ if $c^4 = n^{13/6} (4k/k_{qr})$, where the bracketed term involves the nuclear cores only, since k_{qr} is the sub-period constant of our formula.

It thus appears that independent lines of thought afford support to the form which our empirical relation has taken, and provide evidence that the group number enters into the interrelation of k_e with r_e .

Summary.

Recent theoretical work affords support for the form $k_e r_e^6 n^5 = k_{qr}$ of relation between bond constant k_e and distance r_e , and indicates that the group number n is correctly introduced. The potential function used by Linnett supports the relation with $x = 5$ and $y = \frac{1}{2}$ or $\frac{3}{2}$. Newing's recent work is shown to support the preferable form with $x = 6$, and to be consistent with the assumption that the repulsion term in the potential energy function is of the type ar^{-4} .

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⁴ Newing, *Phil. Mag.*, 1940 (vii), 29, 298.

⁵ Newing, privately communicated.

⁶ Slater, *J. Chem. Physics*, 1933, 1, 687.

THE ACTIVITY COEFFICIENT OF HYDRIODIC ACID AT 25°. FROM ISOPIESTIC VAPOUR PRESSURE MEASUREMENTS.

BY H. S. HARNED AND R. A. ROBINSON.¹

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In recent years we have used both e.m.f. and vapour pressure methods to determine the activity coefficients of a number of electrolytes at 25°, these measurements being extended in some cases over a temperature range. By these methods we have investigated the fifteen alkali chlorides, bromides and iodides, hydrochloric acid and hydrobromic acid, leaving hydriodic acid as the final member of this series. The available data on this electrolyte are meagre. Bates and Kirschman,² from measurements of the partial vapour pressure of hydriodic acid at concentrations between 6 and 10 M., obtained results from which the activity coefficient could be calculated relative to the value at any concentration within this range. At lower concentrations the only investigation appears to be that of Pearce and Fortsch,³ who made e.m.f. measurements on suitable cells over the range 0.005 to 0.25 M. They experienced

¹ Sterling Fellow, Yale University, 1940.

² Bates and Kirschman, *J. Amer. Chem. Soc.*, 1919, 41, 1991.

³ Pearce and Fortsch, *ibid.*, 1923, 45, 2852.

some difficulty in calculating activity coefficients because the value of the standard potential of the silver-silver iodide electrode was doubtful. They gave two sets of activity coefficients based on different reference values at 0.005 M., these two reference values being obtained by comparison with other electrolytes. Redlich and Rosenfeld⁴ obtained a third set of activity coefficients from the same data by using another reference value.

We have now made isopiestic measurements on hydriodic acid at 25° from 0.1 to 3 M., the highest concentration attainable with potassium chloride as reference salt. The determinations are probably not of the standard of accuracy which can be achieved in more favourable cases, such as the comparison of solutions of sodium and potassium chloride.⁵ In the first place, it was necessary to use platinum dishes in place of the silver dishes which we usually employ; platinum has a lower thermal conductivity, and it has been our experience that the attainment of equilibrium is more difficult with platinum than with silver dishes; in the case of hydriodic acid we had to use platinum dishes even for solutions of the lowest concentrations. Secondly, errors may be introduced into these determinations by the instability of hydriodic acid. This acid is, therefore, not an ideal subject for isopiestic measurements but, since little information is available about its activity coefficient, and considerable difficulty will also be experienced in other methods, we have felt it worth while making these measurements. We do not suggest that the activity coefficients now obtained have an accuracy greater than 0.3 % relative to the values adopted for the reference salt; this is approximately one-third the accuracy which can be obtained in the most favourable cases.

Experimental.

Hydriodic acid was prepared from Merck's material by distillation over red phosphorus in a current of nitrogen. The acid was introduced into

TABLE I.—MOLALITIES OF ISOPIESTIC SOLUTIONS OF POTASSIUM CHLORIDE AND HYDRIODIC ACID AT 25°.

m_{KCl}	m_{HI}	m_{KCl}	m_{HI}	m_{KCl}	m_{HI}
0.1115	0.1072	0.8670	0.7326	2.630	1.878
0.1276	0.1238	0.9584	0.8002	2.813	2.003
0.1910	0.1787	1.061	0.8760	2.973	2.083
0.2195	0.2062	1.329	1.063	3.092	2.135
0.2825	0.2617	1.371	1.087	3.275	2.252
0.4934	0.4378	1.419	1.127	3.596	2.434
0.6272	0.5540	1.595	1.239	3.715	2.503
0.7016	0.6013	1.963	1.479	4.124	2.711
0.7240	0.6233	2.140	1.592	4.452	2.882
0.7824	0.6734	2.443	1.788	4.469	2.893
0.8440	0.7178			4.676	3.002

the platinum dishes immediately after the distillation. A further preparation of acid was made each time the dishes were to be refilled. Two or

⁴ Landolt-Börnstein, "Tabellen," 2er. Erg., p. 1118.

⁵ Scatchard Hamer and Wood, *J. Amer. Chem. Soc.*, 1938, 60 3061; Janis, and Ferguson, *Can. J. Research, B*, 1939, 17, 215; Robinson, *Trans. Faraday Soc.*, 1939, 35, 1217.

three runs were found possible with each sample of acid; during this time the acid remained colourless but, if an attempt was made to obtain further determinations from the same sample, a yellow coloration usually appeared, indicating decomposition of the acid. The experimental results are given in Table I, and the osmotic and activity coefficients calculated from these experimental data are given in Table II in the columns entitled $\phi_{\text{obs.}}$ and $\gamma_{\text{obs.}}$.

TABLE II.—OSMOTIC AND ACTIVITY COEFFICIENTS OF HYDRIODIC ACID AT 25°.

<i>m.</i>	$\phi_{\text{obs.}}$	$\gamma_{\text{obs.}}$	$\gamma_{\text{calc.}}^*$	$\gamma_{\text{calc.}}^\dagger$
0.005	—	—	0.931	0.932
0.01	—	—	0.908	0.909
0.02	—	—	0.882	0.883
0.05	0.956	0.845	0.844	0.846
0.1	0.953	0.818	0.819	0.821
0.2	0.969	0.807	0.805	0.807
0.3	0.984	0.811	0.810	0.811
0.5	1.019	0.839	0.840	0.839
0.7	1.057	0.883	0.884	0.881
1.0	1.116	0.965	0.965	0.963
1.25	1.165	1.046	—	1.045
1.5	1.216	1.139	—	1.138
1.75	1.268	1.245	—	1.246
2.0	1.323	1.367	—	1.367
2.25	1.376	1.501	—	1.504
2.5	1.431	1.656	—	1.655
2.75	1.484	1.827	—	1.827
3.0	1.543	2.025	—	2.018
6.0	—	—	—	7.08
7.0	—	10.8 ^(a)	—	—
8.0	—	18.0 ^(a)	—	—
9.0	—	33.9 ^(a)	—	—
10.0	—	64.6 ^(a)	—	—

* Equation 1: $\log \gamma_{\text{calc.}} = -0.5056 \sqrt{c}/(1 + 1.644 \sqrt{c}) + 0.197 c - \log(1 + 0.036 m)$; valid to 1 M.

† Equation 2: $\log \gamma_{\text{calc.}} = -0.5056 \sqrt{c}/(1 + 1.808 \sqrt{c}) + 0.1725 c + 0.0128 c^2 - \log(1 + 0.036 m)$; valid to 6 M.

^(a) Calculated from the data of Bates and Kirschman, relative to

$\gamma = 7.08$ at 6 M.

Discussion.

The activity coefficients obtained for hydriodic acid are higher than any we have yet encountered for I — I electrodes. The position of the activity coefficient curve in relation to the curves for some other electrolytes is shown in Fig. 1, from which it may be seen that the curve for hydriodic acid is even higher than that for lithium iodide. Moreover, the order of $I > Br > Cl$ holds for the halogen acids as for the lithium, sodium and potassium salts.

The high values of the activity coefficient correspond to high values of the parameters of the extended Debye-Hückel equation:

$$\log \gamma = -0.5056 \sqrt{c}/(1 + 0.3288a^\circ \sqrt{c}) + Bc - \log(1 + 0.036 m) \quad (1)$$

where a° is the distance of closest approach of the ions. The best fit with the experimental data is obtained by putting $a^\circ = 5.0$ and $B = 0.197$,

volume concentrations being calculated from the molalities by means of the relation :

$$c/m = 0.9970 - 0.0368 m + 0.0014 m^2.$$

The activity coefficients calculated by equation (1) are given in Table II, in the column headed $\gamma_{\text{calc.}}^{(1)}$. By comparison with the experimental values it may be seen that equation (1) represents the data up to 1 M. within 0.002 in the activity coefficient, a deviation well within the experimental error. The numerical values of the a° and B parameters are the highest yet recorded, being even larger than those for lithium iodide.

It is not possible to find values of a° and B which will represent the data satisfactorily above 1 M. This limitation to the use of equation (1) has been found with most 1-1 electrolytes, and a further extension of the Debye-Hückel equation is necessary, of the form :

$$\log \gamma = -0.5056 \sqrt{c}/(1 + 0.3288 a^\circ \sqrt{c}) + \frac{Bc + Dc^2}{1 - 1 \log(1 + 0.036 m)} \quad (2)$$

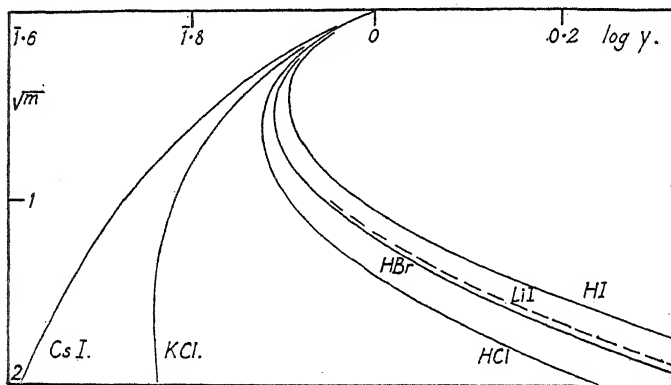


FIG. 1.—Activity coefficient of hydriodic acid in comparison with other 1-1 electrolytes.

By putting $a^\circ = 5.5$, $B = 0.1725$ and $D = 0.0128$, equation (2) can be used up to 3 M. The activity coefficients calculated by this equation are given in Table II, in the column headed $\gamma_{\text{calc.}}^{(2)}$. The calculated values differ from the observed by not more than 0.003, except at the highest concentration, where the deviation is 0.007. It is noteworthy that the values of the distance of closest approach of the ions, as computed by equations (1) and (2), differ by 0.5 Å. This suggests that it will be difficult to obtain an absolute value of this molecular magnitude. Instead, we shall have to content ourselves with a set of comparative values for different electrolytes, using similar methods of computation for results over a common range of concentration.

Having established the validity of equations (1) and (2), we have extrapolated our experimental data to both lower and higher concentrations, in order to determine whether our data are consistent with those of Bates and Kirschman² and Pearce and Fortsch.³ Using equation (1), values of 0.931, 0.908 and 0.882 are obtained for the activity coefficient at 0.005, 0.01 and 0.02 M. respectively. Since these values fall in line

with those obtained for hydrochloric acid ⁶ (0.929, 0.905, 0.876) and hydrobromic acid ⁷ (0.930, 0.906, 0.879), we have some confidence in the application of equation (1) to these low concentrations. Equation (2), gives values 0.001 higher at these concentrations, at 0.1 M. it gives a value 0.003 higher. In view of the experimental error, these deviations are not particularly significant, but it has been found with other electrolytes that equation (1) is somewhat superior to equation (2) in the region of low concentration, and we shall therefore adopt equation (1) for such calculations.

Pearce and Fortsch ³ gave the e.m.f.s of seven cells containing hydriodic acid between 0.005 and 0.25 M., from which the standard potential of the silver-silver iodide electrode may be calculated, provided the corresponding activity coefficients are known. These we calculated by means of equation (1), and then obtained a value of 0.1517 v. for the standard potential, with a probable error of 0.5 mv. This compares reasonably well with that of 0.1522 v. obtained by Owen⁸ by a different method.

Equation (2) may be used to extrapolate the activity coefficient to 6 M., the lowest concentration at which measurements were made by Bates and Kirschman.² In this way a reference value of 7.08 is obtained at 6 M. and the data of Bates and Kirschman at higher concentrations can then be computed relative to this value. These results are also given in Table II.

The activity coefficients at concentrations above 6 M. cannot be computed by equation (2) because the density data necessary for the conversion of molalities to volume concentrations are lacking.

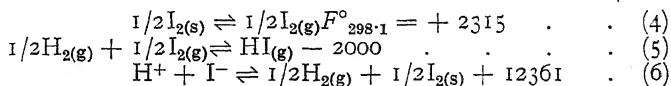
The use of equation (2) for extrapolation as far as 6 M. may be questioned, but support for this procedure is received from the following considerations. The quantity, $p/m^2\gamma^2$, is the equilibrium constant, K , of the reaction :



the evaporation of hydriodic acid from aqueous solution. The partial vapour pressure is known from the data of Bates and Kirschman, and the activity coefficient has been computed, whence it may be shown that $K = 4.16 \times 10^{-10}$, corresponding to a free energy increment,

$$\Delta F^\circ_{298.1} = 12793 \text{ cal.}$$

Lewis and Randall ⁹ have calculated this free energy change by the following series of reactions :



whence, for reaction (3), $\Delta F^\circ_{298.1} = 12676 \text{ cal.}$ This value is 117 cal. lower than that derived above. The first of the three reactions used by Lewis and Randall corresponds to the free energy of sublimation of iodine. Some data have been given recently ¹⁰ for the vapour pressure of solid iodine which can be interpolated between 20° and 30° (by a plot

⁶ Harned and Ehlers, *J. Amer. Chem. Soc.*, 1933, **55**, 2179.

⁷ Harned, Keston and Donelson, *ibid.*, 1936, **58**, 989.

⁸ Owen, *ibid.*, 1935, **57**, 1526.

⁹ *Thermodynamics*, Chap. 37, McGraw-Hill Book Co., New York, 1923.

¹⁰ *I.C.T.*, Vol. III, p. 201.

of $\log p$ against $1/T$ to give $\Delta F^\circ_{298.1} = 2344$ cal. for reaction (4). The second of these reactions has been considered by Murphy,¹¹ who derived an equation for the free energy of dissociation of hydrogen iodide in the gaseous state in terms of spectroscopic data. At 25° this equation gives $\Delta F^\circ_{298.1} = -1897$ cal. for reaction (5). The third reaction corresponds to that in a cell containing hydriodic acid with hydrogen and iodine electrodes. Maitland¹² measured the e.m.f. of 14 cells containing a platinum electrode in solutions of iodine and potassium iodide against a standard calomel electrode and Lewis and Randall used some of these e.m.f.s for calculating the standard potential of the $I_2 - I^-$ electrode. We have repeated this calculation on all fourteen of these measurements and introduced more recent values of the activity coefficient of potassium iodide¹³ to obtain $E^\circ = 0.5352$ v. for this standard potential and $\Delta F^\circ_{298.1} = 12341$ cal. for reaction (6). Lewis and Faragher¹⁴ made measurements on similar cells from which we compute $E^\circ = 0.5356$ v., $\Delta F^\circ_{298.1} = 12350$ cal. Lewis and Randall¹⁵ also give another method involving cells with a lead-lead iodide electrode from which we compute $E^\circ = 0.5347$ v. and $\Delta F^\circ_{298.1} = 12329$ cal. From these three determinations we may write $E^\circ = 0.5352$ v. and $\Delta F^\circ_{298.1} = 12341$ cal. The sum of these three revised results for reactions (4), (5) and (6) gives $\Delta F^\circ_{298.1} = 12888$ cal. for reaction (3) compared with 12793 cal. from the data of Bates and Kirschman. The agreement of these two results, corresponding to an uncertainty of 8 % in γ , is better than would be expected, and gives support to our extrapolation of the Debye-Hückel equation (2) to very concentrated solutions.

Summary.

The activity coefficient of hydriodic acid has been obtained at 25° between 0.05 and 3 M. from isopiestic vapour pressure measurements and the results have been fitted to two forms of the extended Debye-Hückel equation.

These activity coefficients and the e.m.f. data of Pearce and Fortsch lead to a value of $E^\circ = 0.1517$ v. for the silver-silver iodide electrode, compared with 0.1522 v. from other measurements.

One of the Debye-Hückel equations has been used for extrapolation to yield a reference value relative to which the data of Bates and Kirschman can be utilised between 6 and 10 M.

The free energy changes of some hydrogen-iodine reactions have been discussed.

A value of $E^\circ = 0.5352$ v. has been computed for the standard potential of the $I_2 - I^-$ electrode.

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¹¹ Murphy, *J. Chem. Physics*, 1936, 4, 344.

¹² Maitland, *Z. Elektrochem.*, 1906, 12, 263.

¹³ Robinson and Wilson, *Trans. Faraday Soc.*, 1940, 36, 738.

¹⁴ Ref. 9, p. 427.

¹⁵ *Ibid.*, p. 430.

THE YELLOW FLUORESCENT FORM OF ZINC SILICATE.

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*Communication from the Staff of the Research Laboratories of
The General Electric Company Limited, England.)*

Received 6th March, 1941.

In a recent paper describing the results of experiments on the zinc silicate phosphors G. R. Fonda¹ reaches the conclusion that "the yellow phosphor is essentially an amorphous complex of zinc oxide and silica in the orthosilicate proportions." This conclusion is based upon X-ray and other investigations of the products obtained by heat treatment of zinc oxide/silica mixtures, both in the presence and absence of fluxes, at temperatures of 850° C. and about 1500° C. For example, it is claimed that the X-ray diffraction pattern of a material made by heating a mixture of one molecule of zinc oxide and two molecules of precipitated silica at 850° C., with potassium chloride as flux, is identical with that of cristobalite, the high temperature form of silica, apart from diffuse scattering which is ascribed to a "zinc compound of very fine particle size." Again, by rapidly cooling zinc oxide-silica products from 1530° C. the X-ray pattern showed the only crystalline phases to be cristobalite or zinc oxide or both when the yellow fluorescence was observed. Although the rapid cooling method was that described by Schleede and Gruhl² no explanation is offered of the definite X-ray pattern they obtained for a yellow phosphor and which they ascribed to a second crystalline modification of zinc orthosilicate. Fonda's conclusion implies that if such a compound does exist it is in such a fine state of division as to be more logically regarded as an amorphous complex, but such a view is hardly justified if the compound can also be prepared in crystalline condition.

The object of this note is merely to record X-ray evidence of the existence of a crystalline form of the yellow phosphor, and to confirm Schleede and Gruhl's view that there is in fact a second crystalline variety of zinc orthosilicate giving a yellow fluorescence.

Yellow Phosphor prepared at High Temperatures.

Some small scale experiments were first of all carried out using a zinc orthosilicate preparation containing 1 % by weight of manganese and having the normal green fluorescent colour as the starting material. This synthetic silicate had previously been prepared at 1250° C. from a mixture of two molecules of ZnO and one molecule of SiO₂, the manganese being added as chloride. Specimens were placed in very small platinum boats (about 12 mm. long) and heated to various temperatures between 1400° C. and 1550° C. for a few minutes, the boats being subsequently quenched in water. Various degrees of green, yellow, and red fluorescence resulted in the prepared specimens; a temperature of approximately 1500° C.

¹ *J. Physic. Chem.*, 1940, 44, 851.

² Schleede and Gruhl, *Z. Elektrochem.*, 1923, 29, 411.

gave a product whose fluorescence colour was uniformly yellow. This yellow fluorescent phosphor was examined by the X-ray powder method. Its X-ray pattern is reproduced in Fig. 1 (b) and compared with that of the original green

fluorescent zinc silicate, Fig. 1 (a).^{*} It is the pattern of an essentially crystalline substance entirely distinct from the more usual "willemite" type silicate. Examination of the pattern proves that neither cristobalite nor zinc oxide is present in the specimen, although several of the stronger lines appear in very similar positions to certain strong lines of the cristobalite pattern (Fig. 1 (c)). Interplanar spacings measured from the X-ray patterns of this yellow phosphor, cristobalite, and normal zinc orthosilicate are listed in the accompanying table.

Further evidence of the crystalline nature of the yellow phosphor was obtained by examination under a polarising microscope. The material was found to be certainly as anisotropic as the green phosphor from which it had been prepared. A justifiable conclusion is that the yellow phosphor is a second crystalline modification of zinc orthosili-

Interplanar spacings of the lines in the X-ray diffraction patterns of α zinc orthosilicate, α cristobalite, and β zinc orthosilicate (the figures in parenthesis denote rough estimations of intensity by visual inspection).

α Zinc Orthosilicate.	α Cristobalite.	β Zinc Orthosilicate.
7.04 (4)	4.06 (20)	4.39 (2)
4.36 (1)	3.141 (4)	4.10 (5)
4.04 (4)	2.845 (4)	4.04 (2)
3.496 (8)	2.485 (6)	3.939 (2)
3.267 (1)	2.117 (2)	3.703 (2)
3.159 (1)	2.020 (2)	3.646 (5)
2.839 (10)	1.930 (3)	3.502 (6)
2.636 (10)	1.870 (3)	3.332 (1)
2.320 (6)	1.755 (2)	3.238 (5)
2.285 (1)	1.730 (1)	3.067 (3)
2.216 (1)	1.691 (2)	2.846 (8)
2.143 (2)	1.636 (2)	2.531 (6)
2.074 (1)	1.609 (3)	2.493 (6)
2.048 (1)	1.569 (2)	2.454 (3)
2.011 (2)	1.531 (2)	2.398 (2)
1.964 (1)	1.493 (2)	2.313 (2)
1.933 (2)	1.430 (2)	2.250 (2)
1.859 (5)	1.419 (1)	2.210 (4)
1.825 (2)	1.397 (1)	2.150 (2)
1.804 (2)	1.364 (2)	2.114 (4)
1.722 (1)	1.348 (2)	2.053 (2)
1.687 (2)	1.332 (2)	2.022 (4)
1.641 (2)	1.298 (2)	1.967 (1)
1.598 (3)	1.278 (2)	1.947 (2)
1.551 (3)	1.232 (1)	1.918 (1)
1.519 (3)	1.221 (1)	1.880 (1)
1.420 (6)	1.203 (2)	1.855 (2)
1.392 (2)	1.182 (2)	1.777 (2)
1.364 (4)	1.174 (2)	1.729 (1)
1.336 (4)	1.162 (1)	1.686 (2)
1.315 (2)	1.153 (1)	1.660 (1)
1.250 (1)		1.635 (5)
1.227 (1)		1.596 (1)
1.210 (2)		1.580 (2)
		1.559 (3)
		1.531 (1)
		1.517 (4)
		1.488 (3)
		1.446 (3)
		1.430 (3)
		1.420 (3)
		1.406 (2)
		1.394 (2)
		1.371 (2)
		1.344 (2)
		1.329 (2)
		1.309 (2)

^{*} Plate VI. This is the normal zinc orthosilicate pattern apart from a small displacement associated with lattice expansion promoted by solution of manganese.

cate. Hereafter it will be convenient to refer to this modification as β zinc orthosilicate.

The reproduction occurring in Schleede and Gruhl's paper of the X-ray pattern of the yellow phosphor is not a good one, but comparing it with the one reproduced here (Fig. 1 (b)) it is clear that the two X-ray patterns are from substantially similar compounds. Schleede and Gruhl's results on the yellow fluorescent zinc silicate have therefore been effectively repeated.

Some difficulty was experienced in determining the exact conditions under which the yellow phosphor was formed directly from the green fluorescent orthosilicate, and larger scale experiments were carried out with several mixtures containing different proportions of zinc oxide and silica. It was found that consistent results could be obtained most readily when the mixtures contained one or more molecular parts of silica in excess of the orthosilicate ratio. The mixtures containing about 0.5 % Mn as chloride were heated in a tubular electric furnace having a water-cooled extension zone at one end. The boats containing the charge were pushed rapidly into the cool zone after the heat treatment.

Two yellow fluorescent materials were obtained from mixtures containing respectively one and three molecular parts of SiO_2 to one of ZnO on rapid cooling after heat treatment at a temperature of approximately 1450°C . The X-ray diffraction patterns are reproduced in Figs. 1 (d) and 1 (e). These reveal the essentially crystalline nature of the phosphors and show that in each instance there are two phases present, β zinc orthosilicate and cristobalite. The cristobalite phase is considerably greater in quantity in the material prepared from the mixture containing the larger proportion of silica. Since it can easily be shown that the yellow fluorescence is not due to cristobalite it is evidently again associated with the formation of a second crystalline modification of zinc orthosilicate.

Moreover the conclusion that the actual composition of the yellow fluorescing silicate is equivalent to the formula Zn_2SiO_4 is reinforced by the results of the X-ray analyses of these two samples. It might have been argued that, at the high temperature involved in the preparation of the original small specimen from the green fluorescent phosphor, appreciable losses of ZnO could have occurred, sufficient to alter the composition from Zn_2SiO_4 . Comparison of all three X-ray patterns shows, however, just that increase in intensity of the cristobalite phase to be expected if the composition of the yellow fluorescent silicate is substantially Zn_2SiO_4 .

Yellow Phosphor prepared at Low Temperatures.

Our experience with the reaction products of ZnO/SiO_2 mixtures at temperatures between 700°C . and 1000°C . is in some respects similar to that of Fonda's. The major point of disagreement with his conclusions is with regard to the nature of the yellow phosphor itself.

The X-ray diffraction pattern is reproduced in Fig. 1 (f) of a typical yellow fluorescent material made by heat treatment at 850°C . for 3 hours of a mixture of one molecular part of zinc oxide and two of silica (partially dehydrated silica gel) with 0.5 % manganese in the form of manganese chloride. It is quite evident that lines occur for the β form of zinc orthosilicate. The lines are diffuse when compared with those in Fig. 1 (b), thus indicating a very small ultimate particle size, but are sufficiently strong to establish the identity of the compound. A certain amount of non-crystalline material (and possibly a little crystalline cristobalite) may also be present since there is evidence of diffuse scattering on the X-ray pattern, and it is uncertain how much this non-crystalline material contributes to the yellow fluorescence. However, the presence of the finely-divided but crystalline silicate phase accords with the results obtained in the higher temperature range and re-emphasises the conclusion

that the characteristic luminescence can be associated with a definite compound of zinc oxide and silica, an allotropic modification of zinc orthosilicate.

In order to attempt to reconcile these results with Fonda's experiments in the lower temperature range it must be assumed either that the silicate is also actively fluorescent in a relatively non-crystalline condition or that the presence of a poorly crystallised compound was not detectable by the X-ray technique which he adopted. Of these explanations the first appears to be not unlikely, particularly as our experiments have demonstrated a considerable difference in the crystal size of the yellow phosphors prepared respectively at high and low temperatures. But the evidence presented here disproves Fonda's conclusion that in the preparation of the yellow phosphor it is essential to prevent crystallisation. Indeed it is probably worth remarking that the intensity of luminescence is always much weaker for the phosphors prepared in the lower temperature range than for those prepared at high temperatures. This implies that the yellow fluorescence is most intense in instances of most perfect crystal development.

The yellow phosphor is therefore definitely to be regarded as a second crystalline modification of zinc orthosilicate in accordance with Schleede and Gruhl's original conclusion.

Red Phosphor prepared at High Temperatures.

Although several specimens exhibiting red fluorescence have been prepared by high temperature and quenching treatment no evidence was obtained by X-ray analysis of the third crystalline modification of zinc orthosilicate recorded by Schleede and Gruhl. The fluorescence of the specimens was very feeble and the X-ray patterns indicated the presence of only small amounts of crystalline material which could be attributed either to zinc oxide or cristobalite. Until further experimental work has been done the structural identity of the red phosphor must remain an open question.

Summary.

A recent paper by G. R. Fonda on the yellow zinc silicate phosphor is criticised and his conclusion that the yellow fluorescence is necessarily associated with an amorphous complex of zinc oxide and silica is proved to be incorrect.

X-ray examination of the yellow fluorescent materials prepared by rapid cooling of manganese activated zinc oxide-silica mixtures from temperatures of the order of 1500° C. shows that a crystalline zinc silicate, substantially zinc orthosilicate, is present differing in structure from willemite.

The conclusion of Schleede and Gruhl that the yellow phosphor is a second crystalline form of zinc orthosilicate has been confirmed.

The characteristic X-ray diffraction pattern is reproduced and measured interplanar spacings tabulated. It is suggested that this variety of zinc orthosilicate should be referred to as β zinc orthosilicate.

The yellow fluorescent silicate can also be prepared by reaction between zinc oxide and silica at temperatures of the order of 850° C., although relatively poorly developed crystals result.

THE REACTION OF FREE METHYL RADICALS WITH NITRIC OXIDE.

BY J. S. A. FORSYTH.

Received 24th March, 1941.

The inhibition by nitric oxide of the thermal decomposition of many organic compounds has been widely used for detecting reaction chains.¹ Since the relative amount of NO needed to produce maximum inhibition is small, it has been assumed that the inhibiting effect is due to a reaction between the chain-bearing free radicals and the NO. The work described here was designed to attempt a more direct observation of any change produced by NO in the concentration of free radicals present in a decomposing organic vapour.

The removal of metallic mirrors by a stream of free radicals,² a phenomenon later used by F. O. Rice and his collaborators³ to demonstrate the existence of free radicals in the pyrolysis of many organic compounds, seemed to be the most convenient method of measuring concentrations of free radicals. Diethyl ether was selected as a suitable substance to be decomposed; Rice⁴ showed that 90% of the free radicals produced by its pyrolysis were methyl. Also, Staveley and Hinshelwood⁵ found that the rate of decomposition was considerably diminished by the addition of small amounts of nitric oxide.

Experimental.

Ether vapour, at low pressure, was pumped through a long silica tube; it was decomposed by an annular electric furnace, and the rates of removal of tellurium mirrors placed further down the tube were observed. The apparatus is shown in Fig. 1. The ether reservoir, A, was immersed in a Dewar vessel containing a paste of solid carbon dioxide and acetone; at this temperature the vapour pressure of ether is 0.6 mm. Hg. The silica tube, of internal diameter 0.64 cm., was about 70 cm. long, and had a capillary side-arm sealed on at a point 20 cm. from the left-hand end. The reaction products were frozen out in the liquid air trap, C. The appearance of the discharge in the discharge tube, D, was used as an indication of the constancy of the gas pressure; a further check was provided by the small mercury manometer, E. The pumping system consisted of a two-stage mercury pump, backed by a rotary oil pump.

Nitric oxide could be introduced through the capillary side-arm; the gas was made, and stored, in the reservoir, F, by shaking mercury with concentrated H_2SO_4 containing a little concentrated HNO_3 . When required for use, the gas was allowed to pass into the trap, G, which had previously been evacuated (through a by-pass to the pumps, the tap leading into the silica tube being shut). The trap was plugged into a Dewar vessel holding liquid oxygen, so that the NO condensed immediately, as a white solid; if there was any trace of blueness, due to the presence of N_2O_5 , the gas was unfrozen and pumped away, and a fresh lot

¹ Staveley and Hinshelwood, *J. Chem. Soc.*, 1937, 1568.

² Paneth and Hofeditz, *Ber.*, 1929, 62, 1335.

³ F. O. and K. K. Rice, *The Aliphatic Free Radicals*, Baltimore, 1935.

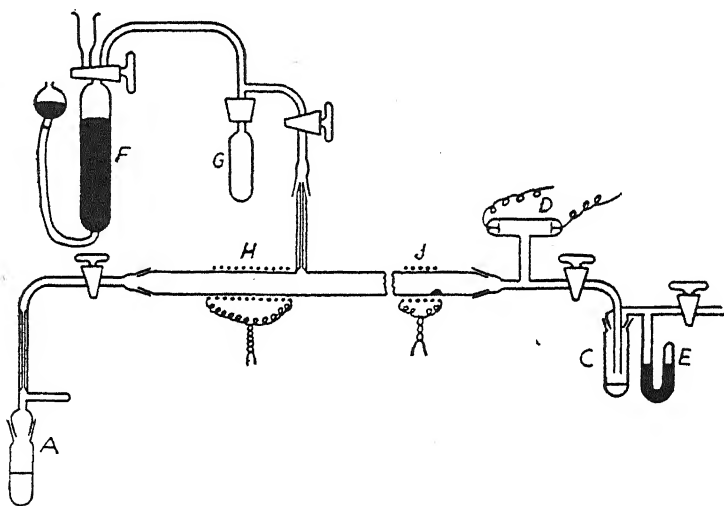
⁴ F. O. Rice, *Trans. Faraday Soc.*, 1934, 30, 152.

⁵ Staveley and Hinshelwood, *Proc. Roy. Soc., A*, 1936, 154, 335.

was made up. When sufficient solid had formed, the reservoir was shut off. The rate of evaporation of the NO into the silica tube was controlled by boiling off the liquid oxygen under reduced pressures, which were measured, stabilised by pumping through a large reservoir.

The ether was decomposed in the furnace, H; a thermo-couple was permanently inserted between the furnace and the tube. The small mobile furnace, J, was used for volatilising a small chip of tellurium; mirrors could thus be deposited at desired points along the tube.

Owing to the difficulty of making accurate standard mirrors, the photo-electric method of Prileshejva and Terenin⁶ was used for determining the rate of removal of mirrors. The left-hand edge of a mirror was always translucent, having been formed from the other side. Light from an ordinary 40-watt bulb shone through the translucent edge, and the intensity of the emergent light was measured by a caesium photo-electric cell. The cell, with its circuit, was mounted inside a box, which was fitted with wheels, and ran along rails laid parallel to the silica tube; the bulb was mounted on an arm extending from the box. So that only light



passing through the centre of the tube should be picked up, the box was provided with a small slit opposite the caesium cell, which was level with the median line of the tube. The light intensity was read off a millivoltmeter. When a mirror was being removed, readings of the millivoltmeter were taken at regular intervals; on plotting \log_{10} volts against time, a curve was obtained whose central portion was straight. This is in accordance with Lambert's law of light absorption; the slope of the central portion of the curve was taken as the rate of removal of the mirror, which will be referred to in the tables as the "activity" (α).

It was found that the mirrors were extremely sensitive to atmospheric oxidation⁷; therefore the silica tube was kept permanently evacuated, and when the ether and NO reservoirs were refilled, air was pumped out through by-passes leading directly to the mercury pump. Impure NO also oxidised the mirrors; hence the necessity of having the solid absolutely white.

⁶ Prileshejva and Terenin, *Trans. Faraday Soc.*, 1935, 31, 1483.

⁷ Cf. Pearson and Glazebrook, *J. Chem. Soc.*, 1937, 567.

The first runs were made to establish the variation of the concentration of the radicals along the tube. The furnace, H, was set at 800° C., and the rates of removal of mirrors at distances between 4 and 25 cm. from the mouth of the furnace were measured. The results are given in Table I.

TABLE I.—RATES OF REMOVAL OF MIRRORS BY FREE RADICALS.

Distance from Furnace, x (cm.).	Rate of Removal, α .	$\log_{10} \alpha$.
6.4	0.34	$\bar{1}.532$
8.4	0.215	$\bar{1}.332$
10.1	0.14	$\bar{1}.147$
9.2	0.17	$\bar{1}.230$
6.0	0.31	$\bar{1}.492$
4.3	0.45	$\bar{1}.654$
13.5	0.08	$\bar{2}.903$
12.6	0.066	$\bar{2}.820$
7.3	0.24	$\bar{1}.380$
5.5	0.345	$\bar{1}.538$
6.8	0.29	$\bar{1}.463$
12.8	0.10	$\bar{1}.000$
24.8	0.016	$\bar{2}.220$
4.2	0.47	$\bar{1}.672$

(Experiments were done in random order, as shown.)

The pressure of the streaming gas was measured by a McLeod gauge attached to the capillary side-arm, while the apparatus was running under standard conditions; the mean value of a number of determinations was 0.226 mm. Hg. The rate of pumping of ether was determined by weighing the ether reservoir before and after a run of known duration (about two hours); the mean value was 1.39×10^{-4} g. for three such runs. The diameter of the tube being 0.64 cm., the streaming velocity of the gas was calculated to be 471.5 cm./sec.

Now, the slope of the line in Fig. 2 is -0.085 , and therefore a distance of 0.301 on the $\log_{10}\alpha$ -axis (corresponding to a drop of 50 % in the concentration) is equivalent to $0.301/0.085 = 3.54$ cm. on the x -axis. This distance is traversed in $3.54/471.5 = 7.5 \times 10^{-3}$ sec., which is the half-life period of the radicals. This value is slightly higher than that given by Paneth and Hofeditz,² namely 5.8×10^{-3} sec., or by Pearson,³ 5.3×10^{-3} sec.; the difference may be due to the nature of the silica surface, or to the diameter of the tube.

³ Pearson, *J. Chem. Soc.*, 1934, 1718.

When the log of the activity is plotted against distance, a straight line is obtained (Fig. 2). This result, indicating that the radicals decay by a process of the first order, agrees with the findings of previous workers in this field; the process is probably a recombination at the wall, ethane being formed.

Decay curves were also obtained for furnace temperatures of 680° and 890° C.; the slopes ($d \log_{10}\alpha/dx$) were approximately the same as that of the previous curve. Mirrors heated to 85° C. were found to be removed at the normal rates (see Fig. 2). That is, the reaction between radicals and tellurium has no appreciable temperature coefficient.

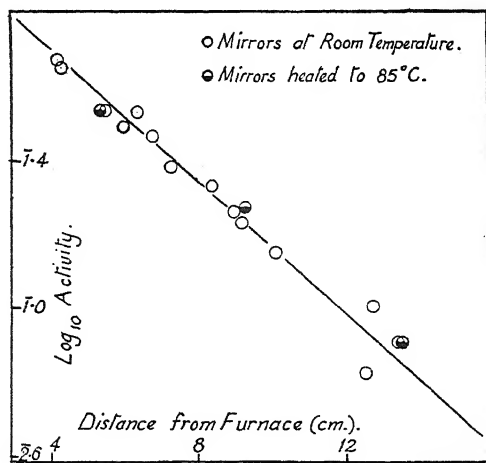


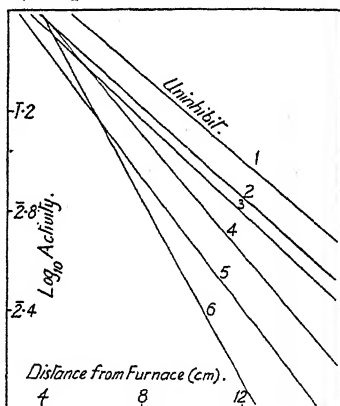
FIG. 2.

The absolute rate of removal was estimated by timing the removal of a mirror of known weight, formed by volatilising a tellurium chip which had previously been weighed; the furnace was placed symmetrically round the chip, so that it could be assumed that the weight of the mirror on either side was equal to half the weight of the chip. The time of removal of 0.0164 g. of tellurium was 24.3 hours, and the mean distance of the mirror from the mouth of the furnace was 12.35 cm.; hence the rate of removal of tellurium was 1.47×10^{-9} g. atoms/sec. Assuming that dimethyl telluride is the product of reaction (for the odour of the condensate in the liquid air trap was typical of that compound, and no trace of the orange-coloured dimethyl ditelluride could be seen), then knowing the rate of pumping of gas (given above), the concentration of free radicals at a point 12.35 cm. from the furnace can be shown to be 1.94×10^{-8} g. radicals per litre.

The effect of NO was next investigated. Decay curves were obtained for radicals in the presence of five different partial pressures of NO, corresponding to pressures of oxygen of 36, 41, 55, 65, and 76 cm. Hg respectively, the temperature of the furnace being maintained at 800° C. throughout. The results are shown in Fig. 3 (the points are omitted, to avoid

FIG. 3.

1. Uninhibited Decay
2. Oxygen Pressure = 36 cm. Hg.
3. " " = 41 " "
4. " " = 55 " "
5. " " = 65 " "
6. " " = 76 " "



confusion), and the line from Fig. 2 is included for comparison. That the lines are still straight shows that the NO does not affect the first order recombination process; it is also seen that the slopes of the lines are related to the amount of NO present. The exact relation will be discussed later.

The rates of pumping of the NO at the various pressures were measured by means of a gas-burette connected to the NO trap. Since the rates were approximately proportional to the vapour pressures of solid NO at the various temperatures (calculated from the results of Dodge and Davis,⁹ and of Henglein and Krüger¹⁰) the pressures of ether and of NO can be taken as independent, and the partial pressures of the latter can be calculated from the rate of pumping of ether at a known pressure. The rates of pumping and the derived partial pressures are given in Table II, along with the slopes of the lines in Fig. 3 ($-d \log_{10} \alpha / dx$).

In Fig. 4 these slopes are plotted against the partial pressures of NO; the graph shows that in the presence of nitric oxide the rate of decay of free radicals ($-d \log_{10} \alpha / dx$) is directly proportional to the partial pressure of nitric oxide. This relationship can be expressed by the equation

$$- \frac{d \log_{10} [\text{CH}_3]}{dx} = k' + k'' [\text{NO}].$$

⁹ Dodge and Davis, *J. Amer. Chem. Soc.*, 1927, 49, 617.

¹⁰ Henglein and Krüger, *Z. anorg. Chem.*, 1923, 130, 181.

TABLE II.

Pressure of Oxygen (cm. Hg.).	Rate of Pumping (c.c./sec.).	Partial Pressure of NO (mm. Hg.).	$-d \log_{10} \alpha / dx.$
36	0.00256	0.014	0.091
41	0.00700	0.038	0.097
55	0.0247	0.132	0.116
65	0.048	0.258	0.138
76	0.117	0.629	0.183

From the graph, k' (the intercept) = 0.091, and k'' (the slope) = 0.155. From these figures it can easily be proved that

$$-\frac{d \log_e [\text{CH}_3]}{dt} = 98.8 + 168.4[\text{NO}] \quad ([\text{NO}] \text{ in mm. Hg.}).$$

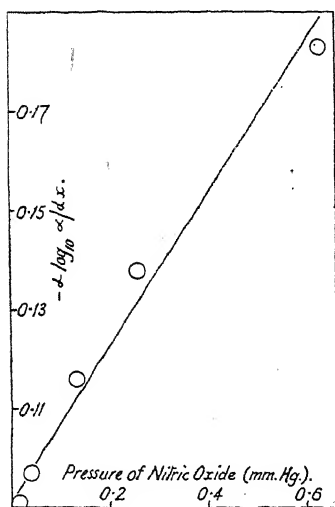


FIG. 4.

Thus the first order spontaneous decay of the radicals has a velocity constant of 98.8 sec.⁻¹, and the reaction of the radicals with nitric oxide has a velocity constant of 168.4 sec.⁻¹ (per mm. Hg NO).

From the foregoing results, we are now in a position to calculate the collision efficiency of the spontaneous decay of the radicals, that of the reaction between radicals and tellurium, and that of the reaction between radicals and nitric oxide.

I. The Spontaneous Decay of the Radicals.—If [radical] = y g. radicals/litre, then the rate of disappearance of radicals is $98.8y \times 10^{-3}$ g. radicals/c.c./second. In the silica tube, 1 c.c. has a wall area of 3.1 sq. cm. The mass of gas striking it, using the familiar collision formula, is $5y \times 10^4$ g. radicals/sec. Therefore

$$\frac{\text{Collisions}}{\text{Reactions}} = \frac{5y \times 10^4}{98.8y \times 10^{-3}} = 5.06 \times 10^5.$$

That is, at room temperature, one radical is removed for every 5×10^5 collisions at the wall.

II. The Reaction between Radicals and Tellurium.—Calculations similar to that given above, show that at the same temperature, one radical is removed for every 360 collisions with a tellurium mirror.

III. The Reaction between Radicals and Nitric Oxide.—Smith and Hinshelwood¹¹ have shown that the inhibition occurs almost exclusively in the gas phase. The collision number for gaseous radicals and NO will be calculated. Let it be assumed, for convenience, that [radical] = 2×10^{-8} g. radicals per litre, and NO = 1 mm. Hg. These

¹¹ Smith and Hinshelwood, *Proc. Roy. Soc., A*, 1939, 175, 131.

values are converted to molecules per c.c., then substituted in the equation

$$Z = n_1 n_2 \sigma_{12}^2 [8\pi RT(1/m_1 + 1/m_2)]^{\frac{1}{2}}$$

Here, σ , the mean molecular diameter, is taken as 3.75×10^{-8} cm.; this value was estimated from the values for CH_4 and NO . This gives the collision number as 1.47×10^{20} per c.c. per second. If each collision were effective, $(1.47 \times 10^{23}) / (6.0 \times 10^{23}) = 0.245$ g. radicals, would be removed per litre second.

Now, since the velocity constant of the reaction is 168.4 sec., the number of g. radicals actually removed per litre per second by NO is

$$168.4 \times 2 \times 10^{-8} \times 1 = 3.368 \times 10^{-6}.$$

Therefore
$$\frac{\text{Collisions}}{\text{Reactions}} = \frac{0.245}{3.368 \times 10^{-6}} = 7.275 \times 10^4.$$

That is, one radical is destroyed for every 73,000 collisions with molecules of nitric oxide.

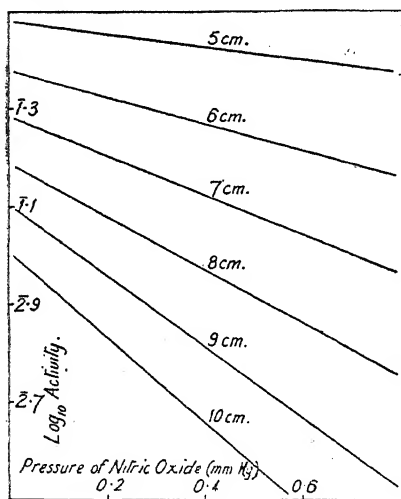


FIG. 5.

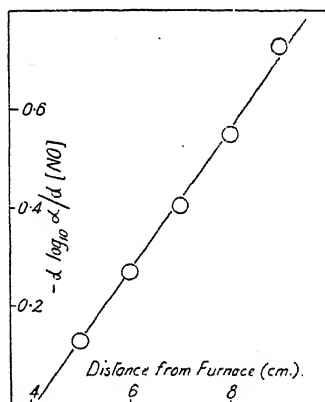


FIG. 6.

But this number $= e^{E/RT}$, where E is the activation energy of the process. Hence, substituting for R and T , E proves to be 6.5 Kcal. Thus the removal of free radicals by NO is a rapid process, even at room temperature. This is direct demonstration that the inhibition of organic decompositions can indeed be due to the immediate reaction of NO with the free radicals which would otherwise have propagated chains.

It is of interest to enquire to what extent the NO removes radicals at various points along the tube. This can be found by measuring the ordinates for various distances in Fig. 3, and plotting the values thus obtained, against the partial pressure of nitric oxide. A series of straight lines, shown in Fig. 5, is found, whose slope is $-d \log_{10} \alpha / d [\text{NO}]$, which may be taken as the inhibiting power of the nitric oxide. The measured slopes are given in Table III, and shown graphically in Fig. 6, plotted against distance.

The fact that the line does not cut the distance-axis at the origin, but at 4 cm., indicates the rather surprising conclusion that no effective destruction of the radicals occurs until a point 4 cm. from the mouth of

the furnace is reached. This can hardly be due to a mixing effect, as complete mixture of the two streams must be very rapid indeed, under the experimental conditions used.

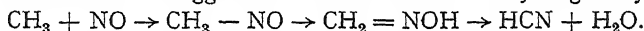
TABLE III.

Distance from Furnace (cm.).	$-\frac{d \log_{10} c}{d[\text{NO}]}$
5	0.13
6	0.27
7	0.405
8	0.55
9	0.73
10	0.88

A chemical explanation can, however, be advanced. The fact that no effective inhibition occurs in the 4 cm. region outside the furnace is equivalent to a virtual displacement of the furnace mouth of 4 cm. to the right. That is, in this short zone, radicals are being formed as rapidly as they are being

destroyed, so that the resultant rate of decay is zero. This can be explained by assuming that the ether molecules retain sufficient energy during this 4 cm. passage to be still capable of decomposition. Thus, although the concentration of radicals which were actually formed in the furnace is diminishing in the normal manner, the loss in concentration is offset by the decomposition of "hot" ether molecules. It should be remembered that since the pressure was only of the order of 1 mm. Hg, and the distance of 4 cm. was equivalent to a time of 8.5×10^{-3} sec., the gas might well remain appreciably hot for this time, after emerging from the furnace.*

Nothing has been said about the products of this reaction. Mitchell and Hinshelwood¹² suggested the formation of hydrogen cyanide:



Indeed, Küchler¹³ claimed to have obtained a positive test for cyanide in the reaction products of the NO inhibited decomposition of C_6H_6 . However, no cyanide could be detected among the products of the experiments described here.

The author would like to thank Professor C. N. Hinshelwood, F.R.S., for his valuable supervision and interest; and Mr. J. D. Lambert and Mr. J. C. Henderson Hamilton, for carrying out certain preliminary experiments.

Summary.

The rate of decay of free methyl radicals (produced by the pyrolysis of a stream of ether at low pressure) both alone and in the presence of small quantities of NO, has been investigated, and from the results it has been calculated that the reaction of radicals with NO has an activation energy of the order of 6.5 Kcal., and is therefore rapid even at room temperature. The rate of decay of the radicals was estimated by the Paneth mirror effect. A value of 7.5×10^{-3} sec. has been obtained for the half-life period of free CH_3 , and certain observations have been made concerning the decay of the radicals.

* A similar "false origin" effect was found to occur when dioxan was decomposed in the same apparatus. The radicals (believed by Küchler and Lambert, *Z. physik. Chem., B*, 1937, 37, 285, to be methylene, CH_2), appeared to decay according to a second order equation, for when the inverse of the activity was plotted against distance from the furnace, a straight line was obtained; which, however, cut the distance-axis at 4.4 cm. That is, the same virtual displacement of the furnace mouth was probably occurring in this case also.

¹² Mitchell and Hinshelwood, *Proc. Roy. Soc., A*, 1937, 159, 32.

¹³ Küchler, *Z. physik. Chem., B*, 1939, 42, 359.

STUDIES IN HYDROGEN OVERVOLTAGE AT HIGH CURRENT DENSITIES. PART III. THE INFLUENCE OF OXYGEN.

By A. HICKLING AND F. W. SALT.

Received 12th March, 1941.

In modern work on hydrogen overvoltage, elaborate precautions are usually taken to exclude oxygen in view of its possible depolarising action at the cathode, and the results of early investigators, who often worked with cells open to the atmosphere, have been severely criticised. During the work described in Part I¹ of this series, it was noted that admission of oxygen to the cell did not appreciably affect the hydrogen overvoltage measurements in the current density range 10^{-3} to 1 amp./sq. cm., and in view of this an attempt has been made to clarify the problem.

The limiting C.D. for the diffusion of a depolariser to an electrode in an unstirred solution at room temperature (17°) is given by²

$$I_{\text{limiting}} = 0.0223 DCn \text{ amp./sq. cm.,}$$

where D is the diffusion coefficient of the depolariser, C its concentration in g. moles/litre, and n is the number of faradays used up by the reaction of 1 g. mole of depolariser at the electrode. The absorption coefficient of oxygen at 17° has the approximate value 0.033, whence $C = 33/22400$ for an aqueous solution in equilibrium with pure oxygen; $n = 4$, and D may be given the approximate value of 0.8 .² Thus the limiting C.D. for the diffusion of oxygen to a cathode in such a solution will be approximately given by $0.0223 \times 0.8 \times 4 \times 33/22400 \approx 10^{-4}$ amp./sq. cm. For a polarising current of this magnitude, therefore, the hydrogen at the cathode may be used up as fast as it is formed and hence no overvoltage will develop. For a C.D. of 10^{-3} amp./sq. cm., however, the depolarising action of the oxygen can at most only account for some 10% of the polarising current, *i.e.* will reduce the effective polarising C.D. from 10^{-3} to 0.9×10^{-3} amp./sq. cm. Now, according to Tafel's equation, which is obeyed at low C.D.'s, the overvoltage is proportional to the log C.D., and for most cathodes a reduction of ten times in the polarising C.D. reduces the overvoltage by approximately 0.1 volt. Hence the decrease in the effective polarising C.D., due to the action of oxygen, would only correspond to a diminution of 0.005 volt in the overvoltage at 10^{-3} amp./sq. cm., which is scarcely appreciable, and for higher C.D.'s the difference should become vanishingly small. Hence diffusion considerations would indicate that the presence of oxygen should be without considerable influence on hydrogen overvoltage measurements down to C.D.'s in the region of the limiting C.D. for oxygen diffusion to the cathode, which for an unstirred oxygen saturated solution would appear to be about 10^{-4} amp./sq. cm., after which the overvoltage should abruptly decrease.

¹ Hickling and Salt, *Trans. Faraday Soc.*, 1940, **36**, 1226.

² Glasstone and Hickling, *Electrolytic Oxidation and Reduction*, 1935, p. 81.

Experimental and Results.

Observations were made at 17° by the method described in Part I, using amalgamated copper cathodes in aqueous $N-HCl$ over the C.D. range $1 - 10^{-5}$ amp./sq. cm. Three sets of experiments were carried out: (a) with a solution carefully freed from oxygen and with the cell filled with pure hydrogen, (b) with the solution saturated with pure oxygen, and (c) with the solution

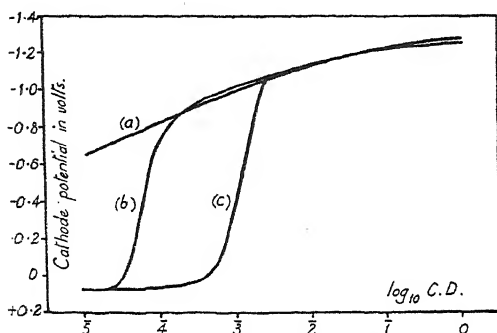


FIG. 1.—Influence of oxygen on hydrogen overvoltage.

the three graphs are identical at high C.D.'s within the limits of probable experimental error. At C.D.'s of approximately 10^{-3} for the stirred, and 10^{-4} amp./sq. cm. for the unstirred, solution, however, the presence of oxygen causes an abrupt disappearance of the overvoltage.

Discussion.

The experimental results are in close agreement with diffusion theory and show conclusively that oxygen is without considerable effect³ on hydrogen overvoltage measurements at C.D.'s equal to or greater than ten times the limiting current for oxygen diffusion to the cathode, *i.e.*, at C.D.'s equal to or greater than 10^{-3} amp./sq. cm. for an unstirred solution in equilibrium with pure oxygen. For a stirred solution, as would be expected theoretically and has been shown experimentally, the value is rather higher, while for an unstirred solution in equilibrium with air the value will be rather less. It thus appears that for the ordinary conditions of hydrogen overvoltage measurement, the presence of oxygen in the cell is quite immaterial at C.D.'s greater than 10^{-3} amp./sq. cm., provided, of course, that time is allowed for the diffusion layer to be set up. At very low C.D.'s, however, the influence of oxygen is very great, and, as found by many workers, the most rigorous precautions must be taken to exclude it if satisfactory overvoltage measurements are to be made.

Exactly similar considerations will apply to other depolarisers which may be present. With alcoholic solvents, for example, it is very difficult to remove all traces of aldehydes, and while these may have considerable influence on hydrogen overvoltage at very low C.D.'s,

³ Over a portion of the potential-log C.D. graph the overvoltage in the oxygen saturated solution would seem to be slightly higher than for the solution free from oxygen, but it is doubtful if the difference is significant in view of possible experimental errors.

as pointed out in Part II,⁴ they may have no effect in the higher C.D. range. Thus in an experiment with an amalgamated copper electrode in N-HCl in ethyl alcohol, the presence of 1 % acetaldehyde (by volume) caused the almost complete disappearance of overvoltage at 10^{-4} amp./sq. cm., but had only a very slight effect on the measurement at 10^{-3} amp./sq. cm. It may perhaps be deemed somewhat unfortunate that in an attempt to avoid other difficulties of overvoltage measurement, much modern work has been carried out at excessively low C.D.'s at which the influence of difficultly removable depolarisers is so very great.

Summary.

1. The influence of the presence of oxygen on hydrogen overvoltage measurements has been investigated, and it has been shown, in agreement with limiting current considerations, that it may be without effect at high C.D.'s, although it causes a complete disappearance of overvoltage at low C.D.'s; at a critical C.D. the transition occurs abruptly.

2. The conclusion is reached that for unstirred aqueous solutions the presence of oxygen is without appreciable influence at C.D.'s equal to or greater than 10^{-3} amp./sq. cm., provided sufficient time has elapsed for the diffusion layer to be set up.

The authors are indebted to the British Association for the Advancement of Science for a grant (to F. W. S.).

University College,
Leicester.

⁴ Hickling and Salt, *Trans. Faraday Soc.*, 1941, 37, 224.

THE SUSPENSION OF SOLIDS IN MIXED LIQUIDS.

BY E. W. J. MARDLES.

Received 7th April, 1941.

Suspensions of finely-divided solids in mixed liquids in their viscosity and dispersion behaviour resemble colloidal solutions of cellulose derivatives, proteins, soaps and resins in mixed liquids; thus, for example, the addition of either kaolin, shellac, cellulose acetate or gelatin to a mixture of methyl alcohol and acetic acid causes an exaggeration of the features of the viscosity-composition curve for the pure liquids. Also, the differences observed in the degree of dispersion of the finely-divided solids with change in the composition of the liquid mixture are often similar to those for the colloidal substances.

In this paper are given data on the viscosity and settling behaviour of some solids in several liquids and in their binary and ternary mixtures and these data throw light on the subject of thixotropy and of the theory of suspensions in general.

Changes in the degree of dispersion of a suspension with change in the composition of the liquid can be conveniently followed (*a*) by noting the sediment volume, *i.e.* the percentage volume occupied by the settled

solid on standing, and (b) by determining the viscosity ratio η/η_0 where η is the viscosity of the suspension and η_0 that of the dispersion medium.

Suspensions in non-polar liquids such as hydrocarbons usually exhibit thixotropy to a marked extent and give large sediment volumes

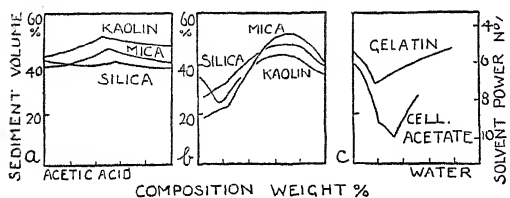


FIG. 1.—Sediment volumes of (a) solids in acetic acid/water; (b) solids in acetic acid/water + 1 % fish glue; (c) solubility of cellulose acetate and gelatin in acetic acid/water; (Mardles, *J.C.S.*, 1924, 125, 2252; *Biochem. J.*, 1924, 18, 215).

with coarser powders such as aluminium powder and samples of silica or mica that settle quickly.

Sediment volumes at 20° C. of kaolin, mica and silica in acetic acid-water mixtures of concentration 15 g./100 c.c. are given in Fig. 1 together with corresponding volumes obtained after adding 1 % fish glue to the suspensions. The settling tests were carried out in glass test tubes of 12 mm. diameter. It will be seen that (a) the sediment volumes of the three solids in the binary mixture form a curve consisting of two intersecting portions, and (b) the addition of the protein causes increased dispersion as indicated by the smaller sediment volumes in the mixtures of higher acetic acid content.

In Fig. 1c are shown solubility data, determined by noting the relative volume of ether required to begin precipitation, for gelatin and cellulose acetate in the liquid mixture and it will be seen that the biggest increase in the dispersion of the suspensions in the mixed liquids containing fish glue coincides closely with the maximum dispersion of gelatin and cellulose acetate.

Some interesting differences were observed in the shapes of the settling curves by varying the kind of solid in the mixed liquids and these differences are shown in Fig. 2.

Similar differences were observed in other mixed liquids as shown in Figs. 2c and 2d for solids in a ternary mixture of benzene, alcohol and acetone. The explanation of these differences involves the shapes of the particles, for during movement the particles tend to orientate along the

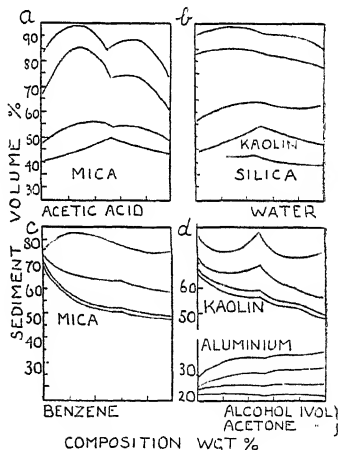


FIG. 2.—Sediment volumes after different intervals of time, namely 5 mm., 10 mm., 1 hour and 15 hours; a, mica, b, kaolin and silica in acetic acid-water mixtures; c, mica, and d, kaolin and aluminium powder in benzene, alcohol and acetone mixtures.

lines of flow; in thinner liquids orientation of the particles occurs more rapidly and by lying less across the stream allows quicker flow or more rapid sedimentation.

Viscosity of Suspensions in Mixed Liquids.

The viscosity ratio η/η_0 has been shown to be dependent on the viscosity of the dispersion medium,² as well as on the degree of dispersion, thin liquids and a high degree of dispersion yielding low viscosity ratios. In Fig. 3 are shown viscosity data for dispersions of kaolin and mica in acetic acid-water mixtures, concentration 15 g./100 c.c., for a gelatin solution and for the pure liquids.

The viscosity-composition curve for the mixed liquids has a maximum in the neighbourhood of 80 % weight acetic acid and the addition either of the solid or of the gelatin causes an exaggeration of the peak; mica has a greater effect than kaolin. The viscosity ratio is greatest in the neighbourhood of maximum viscosity.

Settling of Kaolin in Ternary Mixtures of Liquids.

Kaolin suspensions in binary mixtures of acetic acid and methyl alcohol have already been studied.¹ In Fig. 4a are shown sediment volumes of kaolin in mixtures of water, acetic acid and methyl alcohol; in Fig. 4b the corresponding values when 1 % fish glue was present and in Fig. 4c some solubility data (relative volumes required for precipitation from solution by acetone) for gelatin in the same mixture of liquids.

It will be seen from Fig. 4a that the sediment volume of kaolin in the mixed liquids is greatest in the binary mixture with water containing

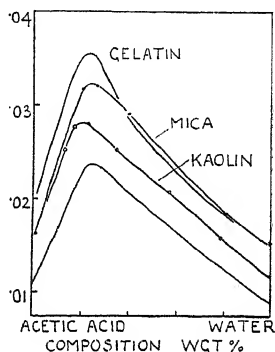


FIG. 3.—The viscosity of suspensions of kaolin and mica in acetic acid-water mixtures, with curve for pure liquids (Dunstan, *J. Chem. Soc.*, 1904, 817) and for gelatin, 0.6 grams/100 c.c. (Mardles, *Biochem. J.*, 1924, 18, 219).

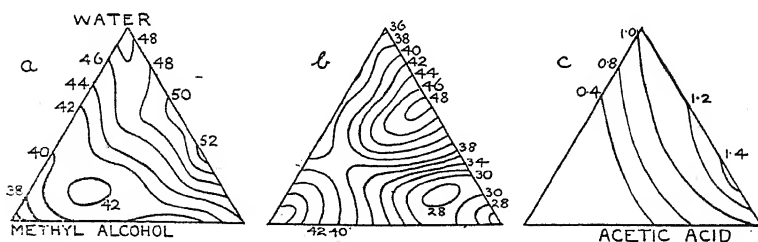


FIG. 4.—Sediment volumes in percentages of kaolin (a) in ternary mixtures of water, methyl alcohol and acetic acid; (b) with the addition of 1 % fish glue; (c) solubility of gelatin in the ternary mixture (solvent power numbers).

about 60 % acetic acid, corresponding to the molecular complex 1 mol acetic acid, 2 mols water, and lowest in methyl alcohol, while a valley runs from a point of about equal volumes of water and methyl alcohol to a point of about 2 volumes acetic acid and one volume methyl alcohol. From Fig. 4b it will be seen that the addition of fish glue has caused a deep depression in the neighbourhood of 67 % acetic acid, 17 % water and 16 %

² Mardles, *Trans. Faraday Soc.*, 1940, 36, 1007.

methyl alcohol, a mixture which has a high dispersive action for gelatin as shown in Fig. 4c.

The sediment volumes in methyl alcohol and mixtures rich in methyl alcohol have slightly increased, due presumably to the lack of dispersion of the fish glue in these liquids, the clay particles becoming sticky with free glue.

Another area in the neighbourhood of the mixture with water containing 40 % acetic acid has also not been much affected.

The suspension of kaolin has been studied in ternary mixtures of ethyl alcohol, acetone and benzene: data as shown in Fig. 5a. In Fig. 5b are shown corresponding data when 0.25 % cellulose acetate was present, and in Fig. 5c are shown solubility data (relative volumes of heptane required to begin precipitation) for cellulose acetate in the same liquid mixtures.

It will be seen from Fig. 5a that the sediment volumes of kaolin in acetone, ethyl alcohol, benzene and their mixtures are greater than in the first mixtures of methyl alcohol, water and acetic acid. There is a depression in the neighbourhood of 2 mols acetone, 2 mols alcohol and 1 mol benzene.

When a small quantity of cellulose acetate was added to the dispersion medium there followed a considerable reduction of the sediment

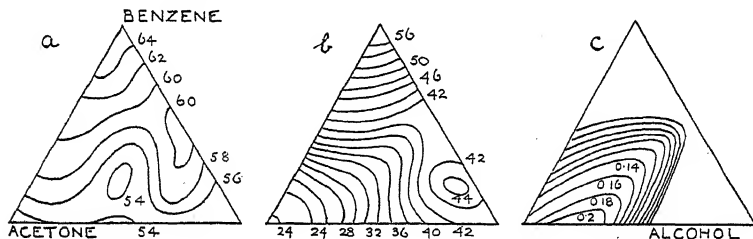


FIG. 5.—Sediment volumes in percentages of kaolin (a) in ternary mixtures of benzene, acetone and ethyl alcohol; (b) with the addition of 0.25 % cellulose acetate; (c) solubility of cellulose acetate in the ternary mixture (solvent power numbers).

volumes especially with the acetone rich mixtures in which the cellulose acetate is readily soluble.

Also the valley running from a point of about 1 mol benzene, 1 mol alcohol to the depression, deepened considerably towards the acetone apex. From Fig. 5c it will be seen that the greatest decreases in sediment volume occurred with the cellulose acetate when in the highest dispersed state.

Rate of Settling.

There are some interesting features in the settling behaviour of the powders in different liquids as indicated by the shapes of the sediment volume-time curves. That these are complex has been reported on by Ward and Kammermeyer³ and by Wirk and Kohler,⁴ who studied the sedimentation of milk of magnesia, calcium carbonate suspensions and other slurries in water.

After shaking the suspensions flocculation initially occurs and finally packing and syneresis of the settled mass. In the less concentrated suspensions and when the degree of dispersion is high the whole of the

³ Ward and Kammermeyer, *J. Ind. Eng. Chem.*, 1940, 32, 622.

⁴ Wirk and Kohler, *ibid.*, 1329.

suspension remains turbid for some time after shaking, although it is possible to observe a settled volume and a more or less clear space at the top of the suspension, both zones not being clearly defined.

The time taken to settle appears to be affected by the sediment volume; this is clearly seen in Fig. 6; in non-polar liquids when the sediment volumes are large the particles fall in clusters, leaving a clear well-defined zone above them, while in polar liquids the particles tend to fall separately and at a much slower rate.

In Fig. 6 are given sediment volumes after various intervals of time for a variety of suspensions. Ostwald and Haller,⁵ who studied sedimentation of bentonite and other solids in numerous liquids, pointed out that density and viscosity of the medium are not sufficient to explain the results but that it is necessary to consider the formation of liquid films at the solid-liquid boundary.

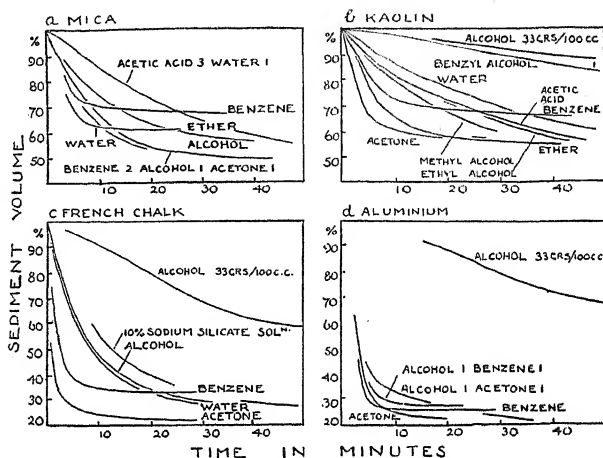


Fig. 6.—Sediment volumes after different intervals of time for (a) mica, (b) kaolin, (c) french chalk, and (d) aluminium powder in various liquids.

From Fig. 6a it will be seen that the rate of fall indicated by sediment volumes of powdered mica during the first few minutes in benzene

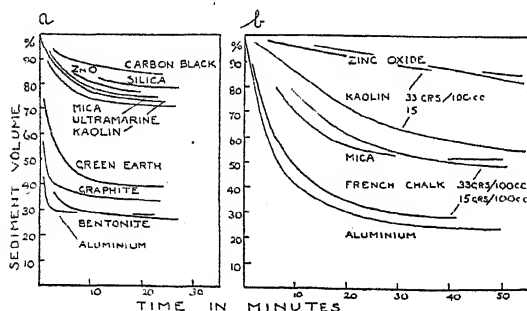


Fig. 7.—Sediment volumes after different intervals of time for solids in (a) benzene and (b) alcohol.

The sample of kaolin in the liquids tried settled most rapidly in acetone (Fig. 6b), which is more viscous than ether; in benzene and methyl alcohol the rate of settling was much different although the

and ether are about the same although the viscosity of ether is about a third that of benzene; in alcohol and the mixture of acetic acid 3 parts, and water, 1 part, the rate of fall is about the same after the first few minutes although the viscosity of alcohol is about half that of the acetic acid mixture.

⁵ Ostwald and Haller, *Kolloid-Chem. Beiheft*, 1929, 29, 354.

viscosities of the liquids are similar. With the other solids, french chalk (Fig. 6c) and aluminium powder (Fig. 6d) the rates of fall were not necessarily inversely proportional to the viscosities of the liquids.

The sediment volumes after different intervals of time for various solids in benzene are shown in Fig. 7a, and in alcohol in Fig. 7b. Usually with those solids of small sediment volume the rate of settling in alcohol and benzene is high. Similarly, with french chalk, using differing concentrations, the rate of settling decreases with rise of concentration, a behaviour observed with suspensions of other solids.

Sediment Volume and Concentration.

As might be expected the sediment volumes on long standing of the suspensions containing various solids were found to be proportional or nearly so to the concentration of the solid dispersed. It will be seen in Fig. 8 that the relationship between sediment volume and vol. % are represented by curves that have but slight curvature over a wide range, although at high concentrations the sediment volume is usually between

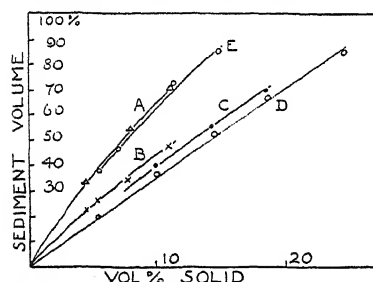


FIG. 8.—Relation between sediment volume and concentration:—

A. Mica in 10 % sodium silicate solution; B. french chalk in 10 % sodium silicate solution; C. aluminium powder in 1 part benzene, 1 part alcohol; D. aluminium powder in acetone; E. kaolin in cyclohexanone.

for 20 cm. 22.5 %; with ultramarine, concentration 20 g./100 c.c., in toluene containing wool fat the sediment volume for a 5 cm. height was 76 % and for a 15 cm. height 71 %.

With bulky settled volumes there are sometimes slow packing changes, thus with a suspension of (a) zinc oxide 40 g. in 100 c.c. of toluene containing wool fat; (b) ultramarine 20 g. in 100 c.c. of the same medium, the decreases in the sediment volumes shown in Table I were observed.

TABLE I.—SEDIMENT VOLUMES OVER A PERIOD OF 60 DAYS.

Days	2	4	6	8	10	20	60
Zinc oxide (per cent.)	87	79	74	—	70	68	67
Ultramarine (per cent.)	66	62	57	53	—	49	48

Silica, aluminium powder, powdered glass wool and other relatively coarse powders in contrast to the zinc oxide settled to practically their final bulk within 48 hours.

Sediment Volume and Viscosity Behaviour.

High and anomalous viscosity behaviour is associated with the phenomenon of thixotropy and with large sediment volumes.

It appeared of interest to inquire whether there is any close relationship between the viscosity behaviour and sediment volume.

In Table II are given the viscosity ratio η/η_0 and sediment volumes for a number of solids dispersed in various liquids and it will be seen that with few exceptions a parallel exists.

TABLE II.—VISCOSITY RATIO AND SEDIMENT VOLUME FOR VARIOUS SUSPENSIONS CONTAINING 7% VOL. SOLID; IN (a) TOLUENE WITH WOOL FAT; (b) BOILED LINSEED OIL; AND (c) RAW LINSEED OIL.

Solid.	(a).		(b).		(c).	
	η/η_0 .	S.V.	η/η_0 .	S.V.	η/η_0 .	S.V.
		%		%		%
Silica	7.9	79	—	—	15.5	71
Carbon black	7.8	78	5.9	73	—	—
Zinc oxide	7.3	72	2.3	65	2.68	69
Mica	2.2	63	2.1	50	—	—
Aluminium	2.15	50	2.0	43	2.45	42
Zinc chrome	1.40	45	1.32	35	1.58	48
Kaolin	1.6	39	1.32	27	—	—
Ultramarine	1.32	38	1.18	24	1.31	43

	η/η_0 .	S.V.
Kaolin in light mineral oil	4.3	% 62
„ benzyl alcohol	2.0	42
„ aniline	1.6	39
„ oleic acid	1.48	38

Summary.

The sediment volumes and some viscosities of suspensions of solids in binary mixtures of liquids and sediment volumes of suspensions of kaolin in two ternary systems have been measured; the sediment volume measurements were repeated with the addition of small amounts of soluble colloidal substances which were found to decrease considerably the volume of settled solid, especially if the added colloid was highly dispersed in the liquid medium.

The data has been discussed in comparison with results obtained with colloidal substances in mixed liquids.

The settling behaviour of the solids in the different liquids was found to be complex; the density and viscosity of the medium are not sufficient to explain the results and it is necessary to take into consideration the degree of flocculation of the solid particles. The shape of the particles also has an important bearing on the rate of fall.

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REVIEWS OF BOOKS.

The Tools of the Chemist. THEIR ANCESTRY AND AMERICAN EVOLUTION. By E. CHILD. (New York: The Reinhold Publishing Corporation. London: Chapman & Hall, Ltd., 1940. Pp. 220. Price 21s. net.)

The author, an English-born American business man, has had the excellent idea of attempting to trace the development of chemical apparatus in America, and including also its mostly European origin. He has dealt with the following topics: people and events in American chemistry; the ancestry and development of the following American chemical laboratory apparatus: balances, glassware, porcelain ware, silica ware, filter paper, heating apparatus, metal laboratory ware, platinum, alundum, rubber ware, and optical apparatus; and in a final section he gives what is known of the history of the firms distributing apparatus in America. The work is well illustrated, including two coloured plates and a hundred and three other illustrations, comprising portraits (many of famous European chemists) and pictures of historical apparatus, reproductions from books, etc. The author has put a great deal of labour into this book and has produced an absorbingly interesting history of chemical apparatus. Although much of it deals with American origins, there is also a large amount of information on early European apparatus, and the point of view is never national. Mr. Child must be numbered among the select few scientific historians who have gone to original sources for their material, and no one who works in a laboratory should fail to be interested and instructed by his book.

J. R. P.

Applied X-Rays. By GEORGE L. CLARK. (London: McGraw-Hill Publishing Co. Ltd., 1941. Price 42s. net.) Pp. 674. Illustrations 342.

Recent years have produced many instances of the way in which X-rays have rendered great service to physical and biological chemistry. Professor Clark in presenting a third edition of his *Applied X-rays* has brought the subject fully up to date, and provided a book of which there is perhaps no counterpart in this country. The reason lies in the particular balance which this volume possesses. Instrumentation is somewhat restricted: the author really does write about what X-rays can do.

The chapter on radiography contains a number of examples which show the capacity of these rays to solve industrial problems. Such are the control of coal-cleaning, the testing of rheological materials, and many more. There are detailed discussions of X-ray photochemistry, crystal-chemistry and polymers; a sound treatment of the technique necessary for the interpretation of diffraction patterns is included.

The section dealing with the X-ray diffraction of liquids is a little less satisfactory. It is impossible to deal with the liquid state without introducing the all-important evidence brought by optical data and the infra-red. It is not so much the *application* of X-rays which matters here, as their power to help in unravelling intrinsic properties.

Many of the illustrations are new, and some of them are remarkably good. A beautiful comparison is that between a photomicrograph and an X-ray pattern for crystalline oxyhaemoglobin.

Professor Clark has earned our gratitude: he has produced a book full to overflowing with information, yet entirely readable.

F. I. G. R.

Physical Chemistry of High Polymeric Systems. By H. MARK.
(Interscience Publishers, Inc. New York, 1940. Pp. vii and 345.
Price \$6.50.)

The average reader of this volume by Professor Mark might be rather puzzled in attempting to correlate the title of the book with the nature of its contents. One might expect a comprehensive account of the application of physical chemistry to the elucidation of the structure and reactions of polymers. It must, however, be emphasised that this book is only one of a series dealing with polymers in general. Volume I was appropriately enough a collection of the published work of the late W. H. Carothers. The volume under review really gives a most useful and very readable account of that part of physical chemistry necessary for a proper understanding of high polymer systems.

Especial prominence is given to the determination of molecular structure. Naturally X-ray technique is well to the fore but dipole moments, spectroscopic and other methods are described in some detail. In addition there is a compact section on modern valency theory. In preparation for the study of solutions of high polymers there is a special section on binary solutions with special reference to the deviations from ideal behaviour. Here, too, there is mention of diffusion and sedimentation in polymer solutions. The kinetics of polymerisation are perhaps unfortunately not dealt with in detail, but that part of the subject is presumably reserved for another volume.

It is not too much to say that this book forms a most valuable introduction to certain parts of physical chemistry from a fresh viewpoint. Readers having no great interest in high polymers will find in it a wealth of interesting information. Those primarily concerned with polymers will gain a balanced insight into the specialised methods used for the investigation of macromolecules.

H. W. M.

The Development of Mathematics. By E. T. BELL. (McGraw-Hill.
1940. Pp. 583. Price 31s. 6d.)

The most convenient way to portray the character of this unusual, if not unique, book is to quote freely from it. In reading it I marked the most striking passages which I should have liked to quote, but I now find that to keep this review to a reasonable length I must restrict myself to quoting only a trivial fraction of these passages.

p. 97. "Unless a man adds something new to mathematics he is not a mathematician."

p. 110. "The ingenious solver of special problems may still be a useful member of mathematical society in that he turns up mysterious phenomena for abler men to strip of their mystery, but he is no longer regarded as a mathematician. This is one line of cleavage between ancient and modern mathematics."

p. 132. "A mathematician creates new mathematics or significantly improves and unifies what already exists. A mathematical physicist as a rule has but little time for purely mathematical pursuits and uses mathematics merely as one of several convenient tools. A theoretical physicist has even less time to devote to mathematics."

"Newton is almost unique in his triple supremacy as a pure mathematician, an applicer of mathematics and an experimentalist."

p. 153. "Another quarter of a century and it had become almost a disgrace for a first-rate mathematician to attack a special problem of the kind which would have engaged Euler in much of his work. Abstractness and generality became the order of the day."

p. 172. "Geometers and algebraists perceived almost simultaneously that mathematical systems are not supernaturally imposed on human beings from without, but are free creations of imaginative mathematicians."

p. 306. "Baseless superstitions, of which the absolute truth of mathematics was one."

p. 343. "A treatise or a monograph on mathematical physics, for example, may be a mass of formulas and equations from beginning to end, and yet make no contribution to mathematics. If the general fact is not obvious, its extreme cases in book keeping or the calculation of characteristic functions in quantum mechanics may illuminate the distinction."

p. 343. "As a further aid to comprehension it is a fair guess that out of a hundred thousand persons picked at random on the streets of New York or Chicago or London or Paris or Moscow or Tokyo not one would know the name of the man whom professional mathematicians almost unanimously have considered the foremost member of their guild since 1912. Many would instantly name a theoretical physicist who deeply resents being called a mathematician."

I wonder if more than one per cent. of the members of the Faraday Society know the answer. In any case these few quotations will serve to show that the relationship between Mathematics (as the word is used by the author and presumably by other modern pure mathematicians) on the one hand and Physics on the other is so distant as to be reminiscent of a song in an American burlesque (1932): "She's the illegitimate daughter of an illegitimate son of an illegitimate nephew of Napoleon." As a physicist writing for readers primarily interested in physics or physical chemistry, all I can say about this book is Koko's initial remark about "the flowers that bloom in the spring."

However, if the editor will allow us to forget that we are physicists and to discuss the book just as we might discuss a book on travel or a biography, my advice to anyone even mildly interested in the subject is to read the book. I have four main reasons for this advice.

Firstly, and obviously, even a cursory reading of the book gives one a vivid general picture of the development of mathematics from the earliest times up to 1940 and a general idea of the significant contributors.

p. 283. "It seems unlikely that posterity will revise the almost universal verdict of 1940 that up till then the three epoch-making mathematicians were Archimedes, Newton and Gauss."

As judged by their influence on the development of pure mathematics the other greatest contributors appear to be Lagrange in the eighteenth century, Abel, Gauß and Cauchy in the nineteenth, Poincaré and Hilbert in the twentieth. The work of Euler and Fourier, on the other hand, would not nowadays be regarded as mathematics by the purists, although this work has been an exceptionally fertile source of work for the latter.

p. 395. "Boole has a strong claim to the sour honour of having been the most greatly underrated mathematician of the nineteenth century."

Secondly, the author has opinions and does not hesitate to express them. In his own words:

p. 512. "If a man has something to say, there is no good reason why he should not say it so that those for whom it is intended cannot possibly misunderstand him, even at the risk of being less polite than is customary at afternoon tea."

Consequently the antithesis in style between this book and the lifeless jargon beloved in the Civil Service recalls, to borrow a phrase recently used by the Prime Minister, the contrast between the atmosphere on the deck of a warship and that in a hothouse. As examples of this refreshing outspokenness:

p. 32. Referring to arithmetical problems set by the ancient Egyptians, "Loaves of bread are partitioned among several imaginary beings in arithmetical progression. There is nothing new, provided it is silly enough, under the sun."

p. 51. "Nor would a mathematical astronomer of the early twentieth century have beheld the astounding spectacle of God masquerading as a mathematician."

p. 488. "The abandonment of the ether except by a few who still find its picturesque contradictions useful."

p. 494. "So successful was the *Methoden* that the weird hybrids 'eigenvalue' and 'eigenfunction' were begotten to oust their all English equivalents that had served for twenty years or more. But working physicists had been too busy to notice them."

Thirdly, an attractive feature of the author's style is a frequent display of wit, which is sometimes, but by no means always, biting. For example:

p. 136. "This is what Zeno and the tortoise knew and neither of them succeeded in clarifying."

p. 164. Describing the novice's impression of the theory of complex numbers: "a beating of an imaginary devil round a supposedly real bush."

There are many other such gems, but I must not anticipate the potential reader's pleasure.

Fourthly, in reading this book one picks up numerous interesting isolated facts, such as the following:

p. 100. The universities of Paris, Oxford, Cambridge, Padua and Naples were all founded between 1200 and 1225.

p. 79. Leap year, adopted by Julius Caesar, was proposed by the Alexandrian Sosigenes.

Cardan's solution of the cubic was discovered by Tartaglia (p. 109); Argand's diagram was first used by Wessel (p. 161); Stokes' theorem was discovered by Kelvin (p. 364); and Laplace's equation was previously used by Lagrange (p. 364). It is a relief to find that in matters of history even mathematicians are inaccurate.

I have only one small complaint regarding the book.

p. ix. "All footnotes are collected for easy reference just before the index." I found the reference anything but easy, because in order to refer to a footnote one must first consult the index to find out the chapter number. This procedure, repeated one or two hundred times, causes a loss of time and patience, which could be avoided by marking the chapter number on every page of the text.

E. A. G.

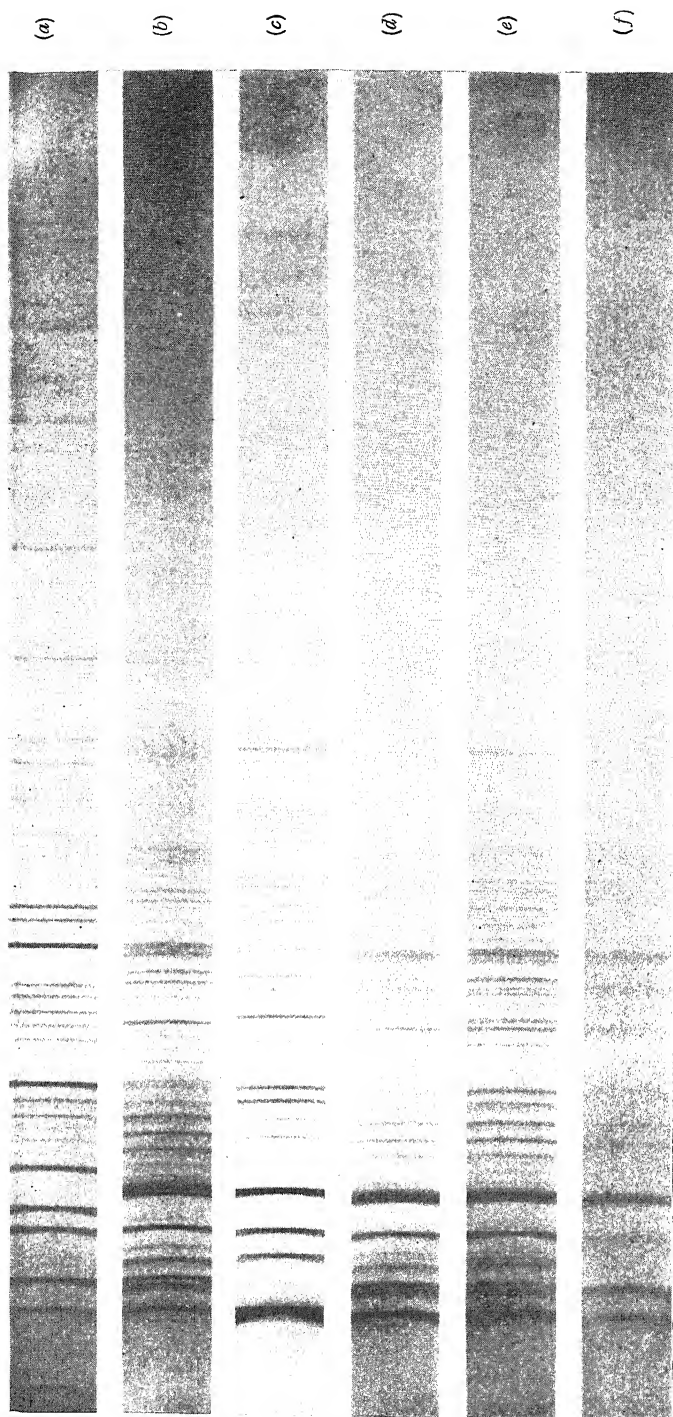


FIG. 1.—X-ray powder photographs of fluorescent zinc silicate preparations, $\text{CuK}\alpha$ radiation, 19 cm. diameter camera. [To face page 310.]

STUDIES IN HYDROGEN OVERVOLTAGE AT HIGH CURRENT DENSITIES: PART IV—THE INFLUENCE OF CONCENTRATION, ANIONS, TEMPERATURE AND CATALYTIC POISONS.

BY A. HICKLING AND F. W. SALT.

Received 22nd April, 1941.

In continuation of the work described in the previous parts of this series,¹ the effects upon hydrogen overvoltage of variation of the concentration and nature of the acid electrolyte, alteration of temperature, and addition of catalytic poisons have been investigated for representative electrodes in the current density range 10^{-3} to 1 amp./sq. cm.

Experimental and Results.

The general experimental method was the same as described in Part I.¹

Influence of Electrolyte.—Observations were made with platinised Pt, W and Hg (amalgamated Cu) electrodes at 16° in 6 N-, N-, and 0.1 N-HCl, and in N-H₂SO₄ and N-H₃PO₄ electrolytes. The results are given in Table I, and are shown in the form of η —log I graphs (η —overvoltage, I —current density) in Fig. 1 A and B. Additional observations were made where necessary to define the shapes of the graphs.

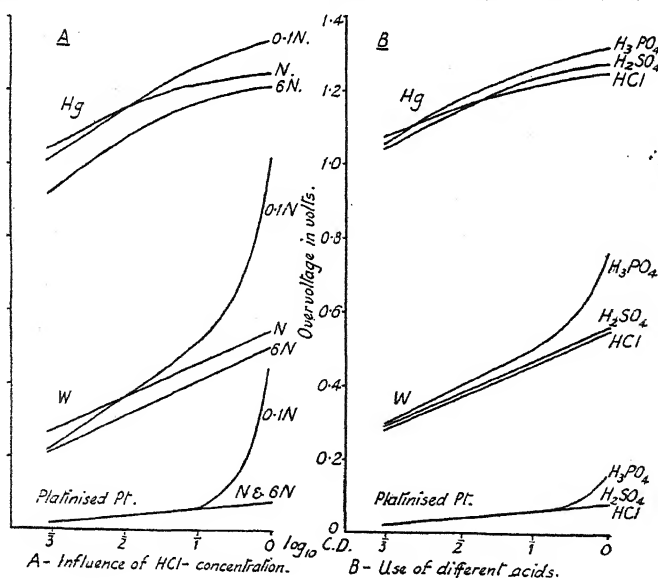


FIG. 1.

¹ Part I, *Trans. Faraday Soc.*, 1940, 36, 1226; Part II, *ibid.*, 1941, 37, 224; Part III (*in press*).

TABLE I.

Electrode.	C.D. Amp./sq. cm.	Overvoltage in volts.				
		Electrolytes—				
		6 N-HCl.	0.1 N-HCl.	N-HCl.	N-H ₂ SO ₄ .	N-H ₃ PO ₄ .
Platinised Pt	10 ⁻³	0.02	0.01	0.01	0.02	0.02
	10 ⁻²	0.04	0.03	0.03	0.04	0.04
	10 ⁻¹	0.06	0.06	0.05	0.06	0.06
	1	0.08	0.55	0.07	0.07	0.15
Tungsten	10 ⁻³	0.21	0.22	0.27	0.29	0.29
	10 ⁻²	0.28	0.36	0.35	0.37	0.39
	10 ⁻¹	0.40	0.51	0.47	0.47	0.50
	1	0.51	1.02	0.54	0.56	0.76
Mercury	10 ⁻³	0.92	1.01	1.04	1.07	1.05
	10 ⁻²	1.07	1.14	1.15	1.15	1.18
	10 ⁻¹	1.16	1.27	1.21	1.24	1.25
	1	1.20	1.32	1.24	1.26	1.31

It is seen that at the highest C.D. in 0.1 N-HCl, and in N-H₃PO₄, where the hydrogen-ion concentration will be relatively low, a sudden increase in the overvoltage of the electrodes takes place. This is undoubtedly due to the onset of concentration polarisation which was expected to occur at high C.D.'s. It may be noted that no concentration polarisation is shown in N-HCl and N-H₂SO₄ even at the highest C.D. employed. Apart from this phenomenon the effect of varying the concentration and nature of the acid is very slight, and it would seem doubtful if any fundamental significance can be attached to it.

Influence of Temperature.—Overvoltage measurements were made with the N-HCl electrolyte at 16° and 17°. The choice of electrodes was limited to those which are not appreciably attacked by the hot acid, and platinised Pt, W, and Hg were chosen as representatives of low, medium and high overvoltage metals, while Sn and Pt were also studied, since these electrodes show marked deviations from Tafel's equation. The Pt and amalgamated Cu electrodes were sealed directly into glass supporting tubes, but with the tungsten and tin electrodes it was necessary to use sealing wax; although the wax softened ² at the higher temperature it did not flow and contamination of the electrode surface did not occur. In general, observations were first made at 16°, then at 70°, and the initial values at 16° were afterwards again checked to ensure that no alteration in the electrode surface had occurred during the work at the higher temperature; in this connection platinum revealed a peculiar behaviour which is referred to subsequently. The results are summarised in Table II, and the η —log I graphs are given in Fig. 2.

At the Hg and Sn electrodes a substantial reduction of overvoltage by about 0.1 volt occurs at the higher temperature, the shapes of the η —log I graphs being largely unaffected; the change would correspond to an average temperature coefficient of approximately -0.002 volt/degree. With the W electrode the decrease in overvoltage increases with rising C.D. but is in any case small, while at the platinised Pt electrode no measurable change of overvoltage occurs on rise of temperature. The behaviour of the smooth Pt electrode was particularly interesting.

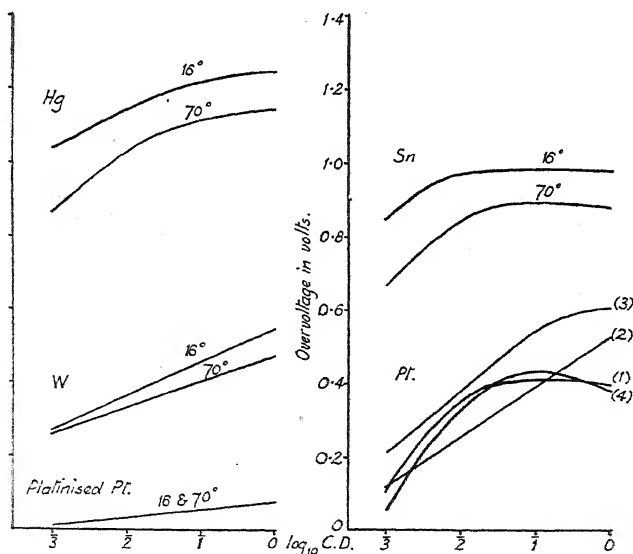
² Other sealing materials, including pitch, Dekhotinsky wax, resin and "Durofix," were tried, but, with the possible exception of resin, they were not appreciably better than sealing wax.

Starting with a fresh Pt wire electrode observations at 16° gave the set of results (1) in Table II and Fig. 2 in reasonable agreement with the values obtained previously in Part I of this series.¹ On passing to 70°,

TABLE II.

Electrode.	Temperature °C.	Overvoltage in volts.			
		C.D. Amp./sq. cm.—			
		10 ⁻³ .	10 ⁻² .	10 ⁻¹ .	1.
Platinised Pt.	16	0.01	0.03	0.05	0.07
	70	0.01	0.03	0.05	0.07
Tungsten	16	0.27	0.35	0.47	0.54
	70	0.26	0.32	0.40	0.47
Mercury	16	1.04	1.15	1.21	1.24
	70	0.86	1.03	1.11	1.14
Tin	16	0.85	0.97	0.98	0.98
	70	0.66	0.85	0.89	0.88
Platinum	16 (1)	0.11	0.35	0.41	0.39
	70 (2)	0.11	0.26	0.40	0.52
	16 (3)	0.21	0.37	0.56	0.60
	16 (4)	0.05	0.33	0.43	0.37

however, the nature of the results was completely changed and set (2) was obtained giving a straight line η — $\log I$ graph. On allowing the cell solution to cool to 16° and checking the initial observations, values

FIG. 2.—
Influence of temperature.

(3) were obtained corresponding to a slightly curved graph. The electrode surface was now observed to be coated with an adherent brownish film, and on removing this by rubbing with filter paper and treatment

with hot HNO_3 , overvoltage values (4) which agreed satisfactorily with (1) were obtained on repeating the observations at 16° . In view of these results it would seem that during the somewhat prolonged electrolyses at the higher temperature (necessitated by the time required for overvoltage at smooth Pt to become substantially constant) a change in the electrode surface occurs which markedly affects the overvoltage behaviour of the metal.

Influence of Catalytic Poisons.—To ascertain the influence of catalytic poisons, the effect of adding small quantities of As_2O_3 , HgCl_2 , and CS_2 to the N-HCl electrolyte at 16° was observed. A platinised Pt cathode was used in general as a representative low overvoltage metal at which reproducible results are readily obtainable, and some further observations were made with a W cathode. To avoid contaminating the usual electrolytic cell, the experiments were carried out in an open beaker, a stream of hydrogen being bubbled through the electrolyte; the work described in Part III¹ has shown that oxygen from the atmosphere is

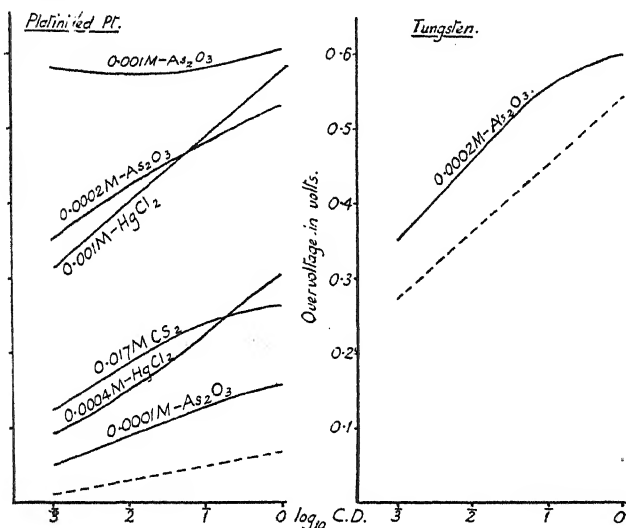


FIG. 3.—
Influence of
Catalytic
Poisons.

without appreciable influence on overvoltage measurements in the C.D. range employed. A calomel half cell, previously directly calibrated against the H electrode in N-HCl , was used as reference electrode. The method of carrying out the observations was then as follows: the freshly prepared cathode was set up in N-HCl and the reproducibility of the usual overvoltage results was first checked in order to ensure that the electrode and electrolyte were free from contamination; successively larger amounts of the poison dissolved in N-HCl were then added, and a set of observations made about 30 minutes after each addition. A selection of numerous results obtained is given in Table III, and the corresponding η — $\log I$ graphs are shown in Fig. 3, the behaviour of the unpoisoned electrodes being indicated by the broken lines.

While it is not claimed that the results are precisely reproducible, there is no doubt of the general tendencies which are very marked. The three poisons listed, even at very low concentrations, raise the overvoltage considerably; this change is usually accompanied by an increase in slope of the η — $\log I$ graph (*i.e.* an increase in the value of the constant b in Tafel's equation) and sometimes the graph becomes curved at the higher C.D.'s, indicating that the overvoltage is tending to a constant value in these cases. With the 0.001M- As_2O_3 electrolyte this state would appear

TABLE III.

Electrode.	Added Poison.	Overvoltage in volts.			
		C.D. Amp./sq. cm.			
		10^{-3} .	10^{-2} .	10^{-1} .	1.
Platinised Pt	(None)	0.01	0.03	0.05	0.07
	As ₂ O ₃				
	0.0001 M	0.05	0.09	0.13	0.16
	0.0002 M	0.35	0.42	0.48	0.53
	0.001 M	0.58	0.57	0.58	0.61
	HgCl ₂				
	0.0004 M	0.09	0.15	0.23	0.31
	0.001 M	0.31	0.39	0.49	0.58
	CS ₂ Satd. soln. (ca. 0.017 M)	0.12	0.19	0.24	0.26
Tungsten	(None)	0.27	0.35	0.47	0.54
	As ₂ O ₃				
	0.0002 M	0.35	0.45	0.57	0.60

to have been reached by the platinised Pt electrode, since the overvoltage is practically independent of C.D. A definite minimum concentration of the poisons seemed to be necessary for an appreciable effect to develop in a reasonable time. Potassium cyanide was also tried as a catalytic poison with the platinised Pt electrode but was found to have only a very slight influence.

Discussion.

A large number of investigations of the effect of hydrogen-ion concentration on overvoltage in the low C.D. range have been made,³ and while the results are not completely satisfactory the experimental evidence shows that in most cases the overvoltage is practically independent of the pH, provided this is not too high.⁴ The results of the present study indicate that the same is true for the higher C.D. range if conditions are such that concentration polarisation does not occur, nor does the nature of the acid electrolyte appear to affect the overvoltage appreciably. The onset of concentration polarisation is clearly indicated by a sudden rise in overvoltage with increasing C.D. and becomes apparent in 0.1 N-solutions of the strong acids at C.D.'s greater than 10^{-1} amp./sq. cm. It is to be noted that these results are free

³ Tafel, *Z. physikal. Chem.*, 1905, **50**, 641; Glasstone, *J. Chem. Soc.*, 1924, **125**, 2646; Sand, Grant and Lloyd, *ibid.*, 1927, 378; Bowden, *Trans. Faraday Soc.*, 1928, **24**, 473; *Proc. Roy. Soc., A*, 1929, **126**, 107; Lloyd, *Trans. Faraday Soc.*, 1929, **25**, 525; Lewina and Zarinski, *J. Physic. Chem. U.S.S.R.*, 1937, **9**, 621; Iofa, *Acta Physicochim. U.R.S.S.*, 1939, **10**, 903. Frumkin (*Z. physikal. Chem., A*, 1933, **164**, 121) has suggested that overvoltage should be independent of pH in pure acid solutions, but should become 0.058 volt greater for each unit increase if a large excess of foreign electrolyte is present; the results of overvoltage measurements in solutions containing large quantities of salts do not seem to support this view (Bowden, *loc. cit.*³; Lewina and Zarinski, *Acta Physicochim. U.R.S.S.*, 1937, **6**, 491; Wagner and Traud, *Z. Elektrochem.*, 1938, **44**, 391; Iofa, Kabanov, Kuchinski and Chistyakov, *Acta Physicochim. U.R.S.S.*, 1939, **10**, 317; Lukowzew, Lewina and Frumkin, *ibid.*, 1939, **11**, 21).

⁴ Bowden and Agar, *Ann. Report*, 1938, **35**, 97.

from resistance error by virtue of the method of measurement employed, and demonstrate unmistakably the effect of concentration polarisation; it has hitherto been difficult⁵ to distinguish clearly between these two factors. The general conclusion reinforces the view put forward in Part II from a study of the influence of the solvent, that the environment of the hydrogen ion is not a primary factor in determining overvoltage.

The influence of temperature on overvoltage has not been investigated very fully, and the published results are often unreliable on account of changes in the electrode surface during the course of measurement.⁶ Thus the temperature coefficient of Zn in H_2SO_4 electrolytes has been variously recorded as -0.00031 and -0.0016 volt/degree.⁷ Knobel and Joy⁸ found that for platinised Pt the temperature coefficient was inappreciable, while for a variety of other metals it had a value of -0.002 to 0.003 volt/degree, and Bircher and Harkins⁹ and other workers⁹ have reported similar values. Bowden¹⁰ has deduced from the activation theory of overvoltage that at constant

current density $\frac{d\eta}{dT} = -\frac{W - \alpha\eta F}{\alpha FT}$, where W is the energy of activation at the reversible potential, α is a constant (usually about 0.5), and F and T have their usual significance. This expression does not seem to have been tested experimentally, except in the case of mercury,¹⁰ and would suggest that the temperature coefficient is dependent upon both the overvoltage and the temperature at which it is measured; for different metals W and η will change together and hence the temperature coefficient might well be approximately constant for different electrodes. On the other hand, Kobosew and Nekrassov¹¹ have deduced from the atomic hydrogen theory of overvoltage that the temperature coefficient should be about -0.002 volt/degree for high overvoltage metals, but very low for the low overvoltage electrodes. The results obtained in the present work would seem to agree approximately with the latter prediction; the values for mercury and tin are of the usual order of -0.002 volt/degree, but at tungsten the temperature coefficient is very small, and at platinised Pt it is not measurable by the present method. According to the activation theory of overvoltage the coefficient b in Tafel's equation should vary directly as the absolute temperature,¹⁰ i.e. the slope of the η -log I graph should increase with rise of temperature; this seems to be so for the initial portions of the graphs for Hg and Sn, but with the W electrode the slope is appreciably less at 70° than at 16° .

The formation of the brown film on smooth Pt at the higher temperature with simultaneous change in the overvoltage behaviour of the metal has certain features in common with the observations of Grant¹² who used Ag cathodes in alkaline solutions at ordinary temperatures. This worker noted that in certain cases a black film formed on the Ag, although rigorous precautions were taken to exclude

⁵ Cf. Bowden and Agar, *loc. cit.*⁴, p. 95.

⁶ Knobel and Joy, *Trans. Amer. Electrochem. Soc.*, 1923, 44, 443.

⁷ Rideal, *J. Amer. Chem. Soc.*, 1920, 42, 94; Westrip, *J. Chem. Soc.*, 1924, 125, 1112.

⁸ *J. Amer. Chem. Soc.*, 1923, 45, 2897.

⁹ Harkins and Adams, *J. Physical Chem.*, 1925, 29, 205; Rideal, *loc. cit.*⁷; Glasstone, *J. Chem. Soc.*, 1924, 125, 2651.

¹⁰ Bowden, *Proc. Roy. Soc. A*, 1929, 126, 107; see also Bowden and Agar, *loc. cit.*⁴, p. 91.

¹¹ *Z. Elektrochem.*, 1930, 36, 529.

¹² Grant, *Trans. Faraday Soc.*, 1928, 24, 226; see also Part I.¹

impurities, and the overvoltage was thereby raised considerably. The cause of these phenomena is not clear, but it seems to be connected with very vigorous gas evolution at the cathode and drastic conditions such as obtain at high current densities and temperatures. It may be noted that the production of such cathodic films by electrolysis at high current densities has been studied by Bredig and Haber,¹³ who conclude that, with Pt, the phenomenon is due to a disintegration of the electrode surface connected with the adsorption of hydrogen, and it is of interest that Bonhoeffer¹⁴ has in some cases obtained similar films by the action of atomic hydrogen on metals, and he suggests that they may result from temporary hydride formation.

Isolated observations on the effect of poisons on overvoltage, which have been made at Pt and Hg cathodes,¹⁵ have shown that in general both the overvoltage and the slope of the η — $\log I$ graph are increased. The results obtained in the present investigation confirm and extend these conclusions, and have further indicated that in some cases the poisons cause a deviation from linearity of the η — $\log I$ graph at high current densities, similar to that observed with certain electrodes in unpoisoned solutions.¹⁶ The occurrence of these deviations when poisons are present with electrodes which normally give straight line graphs seems to indicate that the attainment of an overvoltage independent of current density corresponds to some state of saturation of the cathode surface which is reached at lower current densities when part of the surface is poisoned.

Summary.

1. The effects upon hydrogen overvoltage of variation of the concentration and nature of the acid electrolyte, alteration of temperature, and addition of catalytic poisons have been investigated for representative electrodes in the current density range 10^{-3} to 1 amp./sq. cm.

2. Variation of the concentration of acid and the use of different acids has little influence upon overvoltage except when conditions are such that concentration polarisation occurs; this becomes appreciable in 0.1 N-solutions of strong acids at current densities greater than 10^{-1} amp./sq. cm.

3. Rise of temperature to 70° causes a substantial diminution in overvoltage at Sn and Hg electrodes corresponding to an average temperature coefficient of approximately -0.002 volt/degree; at W only a slight decrease occurs, and at platinised Pt no appreciable change could be detected.

4. The addition of small quantities of As_2O_3 , $HgCl_2$, and CS_2 raises the overvoltage at platinised Pt very considerably; the slope of the overvoltage— \log C.D. graph is also increased, and in certain cases deviations from linearity are observed. Further measurements have been made at a tungsten electrode.

The authors gratefully acknowledge a grant from the British Association for the Advancement of Science (to F. W. S.).

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¹³ *Ber.*, 1898, **31**, 2741; see also Poggendorf, *Ann. Physik*, 1844, **61**, 605; Haber, *Z. anorg. Chem.*, 1898, **61**, 438.

¹⁴ *Z. physikal. Chem.*, 1924, **113**, 199.

¹⁵ Volmer and Wick, *ibid.*, **A**, 1935, **172**, 429; von Náray-Szabó, *Naturwiss.*, 1937, **25**, 12; see also Bowden, *loc. cit.*¹⁰ For earlier work, see, for example, Le Blanc, *Abhdlg. Bunsen-Ges.*, 1910, No. 3; Nutton and Law, *Trans. Faraday Soc.*, 1907, **3**, 50.

¹⁶ See Part I.¹

THE DISSOCIATION OF SULPHURYL CHLORIDE.

By H. W. THOMPSON.

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The dissociation of sulphuryl chloride was first studied by Trautz,¹ who obtained rather erratic values for the equilibrium constant at temperatures in the region 100-200° C. More recently Arie² has re-measured the equilibrium at about 50° C., and has given highly precise expressions for $\log K_p$, for ΔG^0 , the free energy change, and for ΔH , the change in heat content, as a function of temperature. The data of Arie and Trautz show marked differences, and in view of the experimental difficulties involved in these measurements the accuracy claimed by Arie is surprising.

The free energy functions of Cl_2 and SO_2 have been calculated from the molecular data by Giauque,³ and by Cross.⁴ Palmer⁵ has recently determined the dimensions of the SO_2Cl_2 molecule by the method of electron diffraction; the vibration frequencies have also been established from measurements on the Raman spectrum. Sufficient data is therefore available to estimate the free energy, and by combining this with thermochemical data to calculate the equilibrium constant of dissociation of SO_2Cl_2 into SO_2 and Cl_2 . In view of the discrepancies mentioned above, it seemed profitable to compare the constants measured with those calculated.

1. The Free Energy of Sulphuryl Chloride.

The total translational plus rotational entropy is given by

$$S^0_{\text{t.r.}} = 3/2 R \ln M - R \ln \sigma + 4R \ln T + 1/2 R \ln ABC - 9.155,$$

in which M is the molecular weight in grams, σ the symmetry number, and A, B, C are the moments of inertia in units 10^{-40} g. cm.². The translational plus rotational contribution to the free energy function $-(G^0 - E_0^0)/T$ is then $(S^0_{\text{t.r.}} - 4R)$.

According to Palmer, $r_{\text{SO}} = 1.43 \pm 0.02$ Å, $r_{\text{SCl}} = 1.99 \pm 0.02$ Å, $\angle \text{OSO} = 119^\circ 48' \pm 5'$, and $\angle \text{ClSCl} = 111^\circ 12' \pm 2'$, the molecule being a distorted tetrahedron. Taking the most probable dimensions we obtain $ABC = 3.88 \times 10^7$, and $\sigma = 2$.

The Raman spectrum has been studied by Nisi,⁶ Matossi and Aderhold,⁷ Langseth,⁸ and Cabannes and Rousset.⁹ The symmetry class is C_{2v} and the nine normal modes fall into four groups, listed in Table I.

C_2 is the twofold rotational axis of symmetry, σ_x the plane containing the ClSCl angle, and σ_y that containing the OSO angle. The two rocking vibrations involve rocking of the Cl-S-Cl and O-S-O groups with

¹ *Z. Elektr.*, 1908, 35, 543.

² *Inst. Phys. Chem. Res. Tokio*, 10, 32.

³ *J. Am. C.S.*, 1932, 54, 1731; 1939, 61, 1970.

⁴ *J. Chem. Physics*, 1935, 3, 825.

⁵ *J. Am. C.S.*, 1938, 60, 2360.

⁶ *Jap. J. Physics*, 1930, 6, 1.

⁷ *Z. Physik*, 1931, 68, 683.

⁸ *Ibid.*, 1930, 72, 350.

⁹ *Ann. Physique*, 19, 229.

TABLE I.

Class.	Number of Modes.	Polarisation.	Symmetry with respect to			Form.	Designation.
			C_{2v} .	σ_x .	σ_y .		
A_1	4	P	s	s	s	SO valency SCI valency SO ₂ deformation SCI ₂ deformation	ν_1 ν_2 ν_3 ν_4
A_2	1	dp	s	as	as	twisting	ν_5
B_1	2	dp	as	as	s	SO valency rocking	ν_6 ν_7
B_2	2	dp	as	s	as	SCI valency rocking	ν_8 ν_9

respect to each other in planes at right angles to each other. All the frequencies are permitted as fundamentals in the Raman spectrum. It is seen that 4 are polarised and five depolarised.

The frequencies observed are as follows :—

214 (5) polarised	390 (5) depolarised	576 (0) depolarised
280 (2) depolarised	408 (10) polarised	1190 (1) polarised
365 (1) depolarised	560 (5) polarised	1415 (0) depolarised.

The two high frequencies 1190 and 1415 can at once be assigned to the symmetrical (A_1) and antisymmetrical (B_1) valency vibrations of the SO₂ group, the smaller being ν_1 and the larger ν_6 . These correspond to the values 1152 and 1361 of SO₂, and the values 1170-1200 present in the spectra of such molecules as HO.SO₂Cl and H₂SO₄. Of the three other polarised Raman displacements 560, 408 and 214, the value 560 can be assigned to ν_3 , the SO₂ group deformation, similar to the value 526 in SO₂. 408 will then be assigned to ν_2 and 214 to ν_4 .

An unambiguous assignment of the three remaining frequencies cannot be made, but it is very probable that the twisting vibration ν_5 will have the lowest value 280; the two rocking vibrations ν_7 and ν_9 will then have values 365 and 390. Since none of these vibrations is degenerate, the uncertain assignment to the particular vibration types does not affect the subsequent calculations.

The total translational plus rotational entropy is thus found to be $S_{t,r}^0 = 4R \ln T + 21.46$, and the corresponding part of the free energy function $-(G^0 - E_0^0)/T$ is $4R \ln T + 13.51$. The vibrational contributions to the free energy have been calculated on the assumption of harmonic character, using the tables of Wilson.¹⁰ The results are shown in Table II. At 291.16° K. the value of $(H^0 - E_0^0)/T = 7.948 + 4.80 = 12.75$, so that $(H^0 - E_0^0) = 3.71$ kcal. At 298.16° K., $(H^0 - E_0^0)/T = 7.948 + 4.93 = 12.88$, so that $(H^0 - E_0^0) = 3.84$ kcal. The calculated entropy and specific heat at each temperature are also given in Table II. In Table III values of the free energy at the various temperatures for SO₂, Cl₂ and SO₂Cl₂ are listed together. The values for Cl₂ and SO₂ are taken from the papers of Clayton and Giauque and of Cross. The values of $\Delta(G^0 - E_0^0)$ for the dissociation of SO₂Cl₂ at each temperature is then calculated. We now require a value of ΔE_0^0 in order to calculate ΔG^0 and K_p .

¹⁰ Chem. Rev., 1940, 27, 17.

TABLE II.

Temp. °K.	$-(G^0 - E_0^0)/T.$			$S^0.$		$C_{vib.}$	$C_p^0.$
	t.r.	Vib.	Total.	Vib.	Total.		
291·16	58·61	2·65	61·26	7·44	74·00	10·39	18·34
298·16	58·80	2·77	61·57	7·70	74·45	10·56	18·51
300	58·85	2·80	61·65	7·76	74·56	10·60	18·55
303	58·92	2·85	61·77	7·85	74·72	10·67	18·62
323	59·44	3·18	62·62	8·55	75·94	11·11	19·06
380	60·73	4·14	64·87	10·49	79·17	12·19	20·14
400	61·12	4·46	65·58	11·10	80·19	12·51	20·46
410	61·33	4·63	65·96	11·45	80·73	12·66	20·61
450	62·07	5·29	67·36	12·61	82·63	13·21	21·16

At 18° C. the values of $(H^0 - E_0^0)$ for SO_2Cl_2 , SO_2 and Cl_2 are 3·71, 2·455 and 2·135 respectively. Hence for the reaction $\text{SO}_2\text{Cl}_2 = \text{SO}_2 + \text{Cl}_2$ at this temperature, we have $\Delta(H^0 - E_0^0) = 0·88$ kcal. There is a sharp disagreement between different estimates of ΔH for the reaction at 18° C. The equilibrium measurements of Trautz suggest that $\Delta H = 11·2$ kcal., which gives $\Delta E_0^0 = 10·32$ kcal. On the other hand, several sets of thermochemical measurement give 86·2 kcal. for the heat of formation of SO_2Cl_2 gas; and combining the latter value with the heat of formation of SO_2 determined by Eckmann and Rossini¹¹ with high accuracy we obtain $\Delta H = 15·3$, giving $\Delta E_0^0 = 14·42$ kcal. The values of ΔG^0 obtained from each of these values of ΔE_0^0 are given in Table III.

TABLE III.

Temp. °K.	$-(G^0 - E_0^0)/T.$			$\Delta(G^0 - E_0^0).$	ΔG^0		ΔG^0	
	$\text{SO}_2\text{Cl}_2.$	$\text{SO}_2.$	$\text{Cl}_2.$		For	For	Observed.	
					$\Delta E_0^0 = 10.32.$	$\Delta E_0^0 = 14.42.$	Trautz.	Arli.
303	61.77	51.13	46.10	-10.74	-0.42	3.68	—	2.15
323	62.62	51.70	46.55	-11.51	-1.19	2.91	—	1.60
380	64.87	53.10	47.75	-13.68	-3.36	0.74	-0.82	0.00
400	65.58	53.49	48.15	-14.42	-4.10	0.00	-1.29	-0.5
410	65.96	53.72	48.35	-14.80	-4.48	-0.38	-1.51	-0.75
450	67.36	54.51	49.05	-16.29	-5.97	-1.87	-2.38	-1.7

It can be seen that neither set of values agrees very closely with those of either Trautz or Arii. It is therefore profitable to examine the disagreement more closely. If we take $\Delta E_0^0 = 10·32$ kcal., it will be necessary, in order to bring ΔG^0 within the limits of the data of Trautz and Arii, to increase ΔG^0 by approximately 4 kcal. This means that $\Delta(G^0 - E_0^0)/T$ must increase by about 10 cal. The values of $(G^0 - E_0^0)/T$ for SO_2 and Cl_2 are reasonably well established, although that of SO_2 will be slightly modified by anharmonicity. Essentially, therefore, the increase in $\Delta(G^0 - E_0^0)/T$ will have to come from an increase in $-(G^0 - E_0^0)/T$ for SO_2Cl_2 . It is difficult to see how this quantity can be in error by as much as 10 cal. The possible sources of such an error are: (i) inaccurate moments of inertia, (ii) vibrational

¹¹ *Bur. Stand. J. Res.*, 1929, 3, 597.

anharmonicity and other vibrational interactions leading to a non-harmonic vibrational contribution, (iii) the occurrence of a multiplet electronic ground state or several low-lying electronic levels of the molecule, giving an electronic partition function differing from unity. As regards (i), the possible error in molecular dimensions could not produce an error in $(G^0 - E_0^0)/T$ of more than about 0.1 cal.; and the error from vibrational anharmonicity and interactions, although relatively large with such a molecule having several low frequencies of vibration, could surely not exceed 1 cal. and would probably be very much less than this. The remaining large discrepancy would therefore have to come from an electronic contribution to the free energy function $R \ln Q$ in which $Q = \sum p_i e^{-\epsilon_i/RT}$. It is obvious that Q could not be large enough to account for the deficit.

There are several objections to taking the alternative value of ΔE_0^0 , namely 14.42 kcal. Since the calculated values of $(H^0 - E_0^0)$ for reactants and products cannot be appreciably in error, this value of ΔE_0^0 implies a value of ΔH much in excess of that measured by either Trautz or Arie from their studies of the equilibrium.

The most satisfactory way of bringing the calculated values into line with the experimental data may be to take $\Delta E_0^0 = 13.5$ kcal., corresponding to a value of ΔH of 14.4 kcal. at 18° C.; but this leaves unexplained the wide discrepancy between the measured value of ΔH and that just adopted. It is unlikely that variation of ΔH with temperature could account for such a big difference.

In view of the above, it must be concluded that a further experimental study of the SO_2Cl_2 dissociation is desirable. If the heat content change accompanying the reaction could be fixed accurately, it might be possible to reverse the procedure of the above calculations and discover more about the nature of the partition functions for the various degrees of freedom of the SO_2Cl_2 molecule.

Summary.

The known molecular data have been used to calculate statistically the free energy of SO_2Cl_2 , and combining the results with the known free energies of SO_2 and Cl_2 , the equilibrium constants for the dissociation of this substance have been obtained. The calculated values do not agree very well with those measured. Reasons for the discrepancy are discussed. It is concluded that a further study of the equilibrium is desirable.

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THE FREE ENERGY OF METHYL CYANIDE, AND EQUILIBRIUM CONSTANTS OF SOME RELATED REACTIONS.

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It is now recognised that the statistical calculation from molecular data of quantities such as entropy, free energy and specific heat, can lead to values which are frequently more accurate than those hitherto measured. The accuracy is usually limited, however, by insufficient knowledge about vibrational anharmonicity and intramolecular interactions, which in the case of molecules with more than two atoms becomes more important. Unfortunately, the majority of substances of chemical and industrial importance belong to the latter category. It is unlikely that the methods at present available for determining the anharmonic factors and interactions will lead to much progress for a long time; in many cases, too, the errors arising from anharmonicity are small, and when the calculated free energies are used for subsequent calculations of gaseous equilibrium constants, these errors are very often exceeded by inaccuracies in the thermochemical data, such as heats of formation, which are required. Again, in the calculation of equilibria, anharmonic errors in the free energies of reactants and products will to a large extent cancel out. Finally, the errors arising from anharmonicity are sometimes no greater than the possible inexactitude caused by uncertainty in the values of certain fundamental constants.

For these reasons, statistically-calculated values of the several thermodynamic functions, although perhaps not quite exact, must be regarded as useful, particularly as a guide to the possibility of synthesising substances by reactions for which the gaseous equilibrium constants have not otherwise been determined.

Statistical calculations on CH_3Cl and CH_3Br have been made by Kemp and Egan,¹ by Stevenson and Beach,² and by Vold.³ Similar computations on CH_3CN are now summarised, and several equilibria involving this substance are then discussed. In the latter connection, the thermodynamic functions of CH_4 , C_2H_6 , $(\text{CN})_2$, C_2H_4 and NH_3 are calculated. In accordance with the practice of other workers in this field, the fundamental constants used were those in *International Critical Tables*, namely, $R = 1.9869$ cal. degree⁻¹ mole⁻¹, $k = 1.372 \times 10^{-16}$ erg/degree Centigrade, and $N = 6.061 \times 10^{23}$. For the non-linear molecules, the total translational plus rotational entropy of the ideal gas at one atmosphere pressure was calculated from

$$S^0_{\text{t.r.}} = 3/2 R \cdot \ln M - R \ln \sigma + 4R \ln T + \frac{1}{2} R \ln ABC - 9.155,$$

¹ *J. Am. C.S.*, 1938, 60, 2097.

² *J. Chem. Physics*, 1938, 6, 25, 108, 341.

³ *J. Am. C.S.*, 1935, 57, 1192.

in which M is the molecular weight in grams, σ the symmetry number of the molecule, and A, B, C are the moments of inertia in units 10^{-40} g. cm.². The translational plus rotational free energy contribution $(G^0 - E_0^0)/T$ is $(-S_{t.r.}^0 + 4R)$ and the heat content function $(H^0 - E_0^0)/T$ and C_p^0 are 7.948 in cal./moles/degree Centigrade units. The vibrational contributions to the several quantities were calculated by interpolation from the tables of Gordon and Barnes,⁴ and of Wilson.⁵ For cyanogen, a linear molecule, the total translational plus rotational entropy of the ideal gas in the standard state of one atmosphere is given by

$$S_{t.r.}^0 = 3/2 R \ln M + R \ln A + 7/2 R \ln T - R \ln \sigma - 7.628,$$

the free energy function is $(-S_{t.r.}^0 + 7/2 R)$ and the heat content function and specific heat are $7/2 R$.

1. Entropy, Free Energy and Specific Heat of Methyl Cyanide.

The bond lengths determined earlier by Brockway⁶ by the method of electron diffraction have recently been amended by Pauling, Springall and Palmer,⁷ who give $r_{CC} = 1.49 \pm 0.03$ Å, $r_{CN} = 1.16 \pm 0.03$ Å. The methyl group has been assumed to have the same structure as in methane,⁸ giving for the small moment of inertia 5.3×10^{-40} g. cm.². The product $ABC = 4.544 \times 10^4$. The infra-red spectrum has been measured by Coblenz,⁹ by Bell,¹⁰ and by Gordy and Williams,¹¹ and the Raman spectrum by Reitz and Skrabal.¹² The vibration frequencies obtained from this work are 376 (2), 917, 1040 (2), 1370, 1415 (2), 2265,

TABLE I.—METHYL CYANIDE.

°K.	Entropy.			$-(G^0 - E_0^0)/T$		$(H^0 - E_0^0)/T$ vib.	$(H^0 - E_0^0)$	C_{vib}	C_p^0
	$S_{t.r.}^0$	$S_{vib.}^0$	$S_{tot.}^0$	Vib.	Total.				
291.16	55.49	2.368	57.86	0.733	48.28	1.635	2.79	4.40	12.35
298.16	55.68	2.474	58.15	0.774	48.51	1.70	2.88	4.54	12.49
300	55.73	2.495	58.22	0.78	48.56	1.715	2.90	4.58	12.53
350	56.95	3.283	60.14	1.084	50.09	2.199	3.55	5.67	13.62
400	58.02	4.117	62.13	1.412	51.48	2.705	4.26	6.75	14.70
450	58.95	4.976	63.93	1.761	52.76	3.215	5.02	7.78	15.73
500	59.81	5.851	65.66	2.13	53.99	3.724	5.84	8.76	16.71
550	60.55	6.769	67.32	2.523	55.12	4.246	6.71	9.73	17.68
600	61.24	7.602	68.84	2.891	56.18	4.71	7.59	10.53	18.47
650	61.88	8.477	70.35	3.289	57.22	5.19	8.54	11.32	19.27
700	62.46	9.348	71.81	3.689	58.21	5.66	9.52	12.07	20.0
800	63.53	11.033	74.56	4.50	60.08	6.53	11.58	13.40	21.3
900	64.46	12.64	77.11	5.31	61.83	7.33	13.75	14.58	22.5
1000	65.30	14.38	79.68	6.23	63.58	8.15	16.09	15.62	23.6
1100	66.06	15.80	81.86	6.94	65.05	8.86	18.49	16.56	24.5
1200	66.75	17.28	83.93	7.76	66.56	9.53	20.97	17.27	25.2

⁴ *J. Chem. Physics*, 1933, 1, 692.

⁶ *J. Am. C.S.*, 1936, 58, 2516.

⁸ *J. Chem. Physics*, 1935, 3, 668.

¹⁰ *J. Am. C.S.*, 1935, 57, 1023.

¹¹ *J. Chem. Physics*, 1935, 3, 664; 1936, 4, 85.

¹² *Wien. Ber.*, 1937, 140, 398.

⁵ *Chem. Rev.*, 1940, 27, 17.

⁷ *Ibid.*, 1939, 61, 927.

⁹ *Carneg. Inst. Publ.*, 1905, p. 35.

2942, 3077 (2). The symmetry number $\sigma = 3$ and the total translational plus rotational entropy is $S_{\text{t.r.}}^0 = 4R \ln T + 10.39$. The remainder of the calculation is summarised in Table I. The units are cal./degree Centigrade/moles, except for $(H^0 - E_0^0)$ which is expressed in kcal. per mole.

Taking values of the heats of formation from Bichowsky and Rossini,¹³ the value at 18° C. of $-\Delta H$, the heat evolved in the reaction

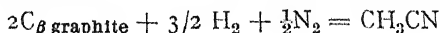


TABLE II.

°K.	ΔG^0 .	°K.	ΔG^0 .
300	24.11	600	29.0
350	24.85	700	30.8
400	25.63	800	32.6
450	26.44	900	34.5
500	27.26	1000	36.3
550	28.12	1100	38.3
		1200	40.2

is -19.84 kcal. At the same temperature the values of $(H^0 - E_0^0)$ for β graphite, hydrogen and nitrogen are 0.239, 1.975 and 2.024 kcal./mole. Hence for this reaction $\Delta(H^0 - E_0^0) = -1.66$, and therefore $\Delta E_0^0 =$

21.50 kcal. Using the free energies for β graphite, H_2 and N_2 given by Clayton and Giaque,¹⁴ the free energy of formation of CH_3CN from β graphite has been calculated between 300-1000° K., and the results are summarised in Table II.

2. Equilibria Involving Methyl Cyanide.

It is now possible to obtain approximate values for the equilibrium constants of certain gaseous reactions involving CH_3CN . In all cases, the accuracy will be determined almost entirely by the value taken for the heat of formation of CH_3CN . According to Bichowsky and Rossini, this value is -19.4 kcal. Conversely, an experimental determination of any of the equilibrium constants might be used to check this heat of formation.

(a) The reaction: $CH_4 + C_2N_2 \rightleftharpoons CH_3CN + HCN$.

According to Bichowsky and Rossini, the heats of formation at 18° C. of CH_4 and $(CN)_2$ are 18.24, -71.0 kcal. per mole. For hydrogen cyanide, Gordon¹⁵ has given the value -30.7 kcal. Thus at 18° C., $-\Delta H$, the heat evolved in the above reaction, is 2.66 kcal. The free energy function and heat content of HCN have been calculated by Gordon with considerable accuracy over a wide range of temperature. The corresponding quantities for CH_4 have frequently been discussed,¹⁶ but there does not appear yet to be a satisfactory tabulation of the results based upon the most recent estimates of the molecular structure. The various functions for this molecule have therefore been recalculated

¹³ *Thermochemistry* (Rheinhold), 1936.

¹⁴ *J. Am. C.S.*, 1930, **52**, 4816; 1932, **54**, 2622; 1933, **55**, 5071.

¹⁵ *J. Chem. Physics*, 1937, **5**, 30.

¹⁶ Frank and Clusius, *Z. physik. Chem. B*, 1937, **36**, 291; Kassel, *J. Chem. Physics*, 1936, **4**, 276; Kassel, *J. Am. C.S.*, 1933, **55**, 1351; Vold, *ibid.*, 1935, **57**, 1192.

and are collected in Table III. The moments of inertia, determined by Ginsburg and Barker,¹⁷ are taken as 5.298×10^{-40} g. cm.², the symmetry number is 12, and the vibration frequencies 1304 (3), 1520 (2),

TABLE III.—METHANE.

°K.	Entropy.			$-(G^0 - E_0^0)/T$		$(H^0 - E_0^0)/T$ vib.	$(H^0 - E_0^0)$	C_{vib}	C_p^0
	$S_{t.r.}^0$	$S_{vib.}$	$S_{tot.}$	Vib.	Total.				
291·16	44·243	0·095	44·34	0·013	36·308	0·082	2·338	0·53	8·48
298·16	44·432	0·105	44·54	0·014	36·498	0·091	2·397	0·59	8·54
300	44·481	0·108	44·59	0·014	36·547	0·094	2·412	0·61	8·55
350	45·707	0·239	45·95	0·036	37·795	0·202	2·852	1·14	9·03
400	46·768	0·433	47·20	0·073	38·893	0·359	3·323	1·78	9·73
450	47·704	0·681	48·38	0·126	39·882	0·554	3·826	2·47	10·42
500	48·565	0·976	49·54	0·197	40·814	0·780	4·364	3·17	11·12
550	49·300	1·316	50·62	0·283	41·635	1·032	4·939	3·89	11·84
600	49·991	1·679	51·67	0·383	42·426	1·296	5·546	4·60	12·54
650	50·628	2·103	52·73	0·501	43·181	1·602	6·207	5·28	13·22
700	51·217	2·491	53·71	0·625	43·894	1·866	6·87	5·93	13·87
750	51·765	2·925	54·69	0·763	44·580	2·162	7·58	6·55	14·50
800	52·278	3·37	55·65	0·915	45·245	2·455	8·32	7·16	15·11
900	53·214	4·275	57·49	1·235	46·501	3·040	9·89	8·27	16·22
1000	54·052	5·19	59·24	1·588	47·692	3·605	11·55	9·27	17·21
1100	54·809	6·12	60·93	1·96	48·82	4·16	13·32	10·16	18·1
1200	55·501	7·03	62·53	2·34	49·90	4·69	15·16	10·95	18·9
1300	56·137	7·96	64·10	2·75	50·94	5·21	17·11	11·64	19·6
1400	56·727	8·82	65·55	3·14	51·92	5·68	19·08	12·24	20·2
1500	57·279	9·69	66·97	3·55	52·88	6·14	21·14	12·77	20·7

2915, 3022 (3).¹⁸ The total translational plus rotational entropy of the ideal gas at one atmosphere pressure is given by $S_{t.r.}^0 = 4R \ln T - 0.858$ cal. per degree per mole. The values in Table III are given with greater

TABLE IV.—CYANOGEN.

°K.	Entropy.			$-(G^0 - E_0^0)/T$		$(H^0 - E_0^0)/T$ vib.	$(H^0 - E_0^0)$	C_{vib}	C_p^0
	$S_{t.r.}^0$	$S_{vib.}$	$S_{tot.}$	Vib.	Total.				
291·16	52·51	5·07	57·58	1·92	47·47	3·155	2·944	6·54	13·50
298·16	52·67	5·23	57·91	2·00	47·71	3·237	3·038	6·65	13·60
300	52·72	5·26	57·98	2·01	47·77	3·254	3·062	6·67	13·63
350	53·79	6·34	60·13	2·55	49·39	3·79	3·76	7·32	14·27
400	54·72	7·45	62·17	3·16	50·92	4·29	4·50	7·85	14·80
450	55·53	8·30	63·84	3·62	52·20	4·68	5·24	8·28	15·23
500	56·29	9·20	65·49	4·13	53·47	5·07	6·01	8·68	15·64
600	57·54	10·85	68·39	5·12	55·71	5·73	7·61	9·37	16·32
700	58·61	12·33	70·94	6·04	57·70	6·29	9·27	9·96	16·91
800	59·54	13·66	73·20	6·89	59·47	6·77	10·98	10·47	17·43
900	60·56	14·97	75·52	7·75	61·15	7·22	12·75	10·91	17·87
1000	61·09	16·13	77·22	8·52	62·66	7·61	14·56	11·29	18·25

precision than those of CH_3CN , since errors arising from anharmonicity or inaccurate moments of inertia must in this case be very small.

¹⁷ *J. Chem. Physics*, 1935, 3, 668.¹⁸ Spöner, *Molekülspektren*, p. 82.

Stevenson¹⁹ has given values for the free energy function of $(\text{CN})_2$ at a few relatively low temperatures, based upon the moment of inertia 175×10^{-40} g.cm.². The tentative vibrational assignment assumed by him, namely 230 (2), 510 (2), 850, 2150 and 2330, has recently been substantiated by the specific heat measurements of Burcik and Yost,²⁰ and of Stitt.²¹ For the purpose of our present calculations, Stevenson's

TABLE V.

°K.	$A(G^0 - E_0^0)/T$	$(\Delta G^0 - \Delta E_0^0)$	ΔG^0	K_p
300	-5.113	-1.534	-3.864	6.5×10^2
400	-4.727	-1.891	-4.221	2.0×10^2
500	-4.552	-2.276	-4.606	1.0×10^2
600	-4.415	-2.649	-4.979	6.5×10
700	-4.328	-3.03	-5.36	4.7×10
800	-4.278	-3.422	-5.752	3.7×10
1000	-4.238	-4.238	-6.568	2.7×10

figures have been extended to higher temperatures. It is clear that at the highest temperatures the values calculated will be somewhat in error, but such errors will not seriously affect the main results of the calculations on equilibria, and may well be outweighed by inaccuracy in the values now taken for the heats of formation. The symmetry number is 2, and the total translational plus rotational entropy at one atmosphere is given by $S_{t,r}^0 = 7/2 R \ln T + 13.044$. The remaining

TABLE VI.

°K.	$A(G^0 - E_0^0)/T$	ΔG^0	K_p
300	-0.736	4.12	1×10^{-3}
400	-0.692	4.063	6×10^{-3}
500	-0.847	3.917	1.9×10^{-2}
600	-1.016	3.73	4.4×10^{-2}
700	-1.212	3.49	8.1×10^{-2}
800	-1.404	3.22	1.3×10^{-1}
1000	-1.87	2.47	2.9×10^{-1}

computations are collected in Table IV.

Combining the data of Tables I, III and IV with those of Gordon for HCN, we have for reaction (a) at 18° C., $\Delta(H^0 - E_0^0) = -0.33$ kcal. Hence $\Delta E_0^0 = -2.33$ kcal. The

free energy data then lead to values of $\Delta G^0 = -RT \ln K_p$ for the reaction, and hence to K_p . Table V summarises the results at a series of temperatures.

(b) The reaction: $2\text{CH}_4 + \text{C}_2\text{N}_2 \rightleftharpoons 2\text{CH}_3\text{CN} + \text{H}_2$.

Using the heats of formation quoted above, at 18° C. we have $-\Delta H = -4.28$ kcal., and $\Delta(H_0 - E_0^0) = -0.06$ kcal., so that $\Delta E_0^0 = 4.34$ kcal. Table VI gives the resulting equilibrium constants.

(c) The reaction: $\text{C}_2\text{H}_4 + 2\text{HCN} \rightleftharpoons 2\text{CH}_3\text{CN}$.

As in the case of CH_4 discussed above, the thermodynamic functions of C_2H_4 have been compiled by several workers,²² but the data are

¹⁹ J. Chem. Physics, 1939, 7, 171.

²⁰ Ibid., III4.

²¹ Ibid., III5.

²² Pitzer, J. Chem. Physics, 1937, 5, 473; Egan and Kemp, J. Am. C.S., 1937, 59, 1264; Kassel, J. Chem. Physics, 1936, 4, 435; Teller and Topley, J. Chem. Soc., 1935, 885; Kassel, J. Am. C.S., 1933, 55, 1351; Smith and Vaughan, J. Chem. Physics, 1934, 3, 697.

scattered and incomplete, and are usually based on earlier values of the moments of inertia and upon erroneous vibrational assignments.

TABLE VII.—ETHYLENE.

°K.	Entropy.			$-(G^0 - E_0^0)/T$		$(H^0 - E_0^0)/T$ vib.	$(H^0 - E_0^0)$	C_{vib}	C_p^0
	$S_{t.r.}^0$	$S_{vib.}^0$	$S_{tot.}^0$	Vib.	Total.				
291.16	51.630	0.589	52.22	0.103	43.785	0.486	2.456	2.33	10.28
298.16	51.819	0.650	52.47	0.117	43.988	0.533	2.527	2.50	10.45
300	51.868	0.666	52.53	0.120	44.040	0.546	2.548	2.55	10.50
350	53.094	1.137	54.23	0.230	45.376	0.908	3.100	3.72	11.67
400	54.155	1.733	55.89	0.380	46.587	1.353	3.720	5.00	12.95
450	55.091	2.390	57.48	0.567	47.710	1.823	4.40	6.16	14.11
500	55.952	3.103	59.05	0.785	48.789	2.318	5.13	7.26	15.21
550	56.687	3.837	60.52	1.028	49.767	2.809	5.92	8.28	16.22
600	57.376	4.592	61.97	1.291	50.719	3.301	6.75	9.20	17.15
650	58.015	5.365	63.38	1.577	51.644	3.788	7.63	10.06	18.01
700	58.604	6.15	64.75	1.878	52.534	4.27	8.55	10.88	18.3
800	59.665	7.68	67.35	2.508	54.225	5.18	10.50	12.30	20.2
900	60.601	9.11	69.71	3.17	55.82	5.94	12.50	13.56	21.5
1000	61.439	10.69	72.13	3.84	57.33	6.85	14.80	14.67	22.6
1100	62.196	12.14	74.34	4.54	58.79	7.60	17.11	15.64	23.6
1200	62.888	13.44	76.33	5.18	60.12	8.26	19.45	16.44	24.4
1300	63.524	14.88	78.40	5.92	61.50	8.96	21.97	17.22	25.2
1400	64.114	16.19	80.30	6.61	62.78	9.58	24.52	17.87	25.8
1500	64.666	17.45	82.11	7.29	64.01	10.16	27.16	18.44	26.4

Analysis of certain infra-red absorption bands²³ has now fixed the moments of inertia as 5.70, 33.2 and 27.5×10^{-40} g. cm.². The magni-

TABLE VIII.

°K.	$\Delta(G^0 - E_0^0)/T$	ΔG^0	K_p
300	28.662	-23.81	2.2×10^{17}
500	30.501	-17.16	3.1×10^7
600	31.101	-13.75	1.0×10^8
800	31.891	-6.90	7.7×10
1000	32.19	-0.22	1.1

TABLE IX.

°K.	$\Delta(G^0 - E_0^0)/T$	ΔG^0	K_p
300	4.378	7.98	1.6×10^{-6}
500	3.705	8.52	1.9×10^{-4}
600	3.399	8.71	7.1×10^{-4}
800	2.874	8.97	3.5×10^{-8}
1000	2.37	9.04	1.1×10^{-2}

²³ Thompson, *Trans. Faraday Soc.*, 1939, 35, 697; Smith, *J. Chem. Physics*, 1940, 8, 798.

²⁴ *Proc. Roy. Soc. A*, 1939, 172, 172.

²⁵ *J. Chem. Physics*, 1940, 8, 970.

²⁶ *Ibid.*, 1941, 9, 118.

Kemp and Egan.²⁷ With the symmetry number $\sigma = 4$, the total translational plus rotational entropy is given by $S_{t.r.}^0 = 4R \ln T + 6.529$. The remainder of the calculations are summarised in Table VII.

Taking heats of formation at 18° C. from Bichowsky and Rossini, we have for reaction (c) $-\Delta H = 33.6$ kcal. Also at this temperature $\Delta(H^0 - E_0^0) = -1.19$ kcal. Hence $\Delta E_0^0 = -32.41$ kcal. The resulting values of ΔG^0 and K_p are given in Table VIII.

TABLE X.—ETHANE.

°K.	291.16	298.16	300	400	500	600	700	800	900	1000
Entropy.										
$S_{t.r.}^0$	52.223	52.412	52.461	54.748	56.545	57.971	59.197	60.258	61.194	62.032
$S_{vib.}^0$	0.605	0.67	0.681	1.875	3.496	5.387	7.368	9.397	11.458	13.476
S_{free}^0	2.899	2.922	2.928	3.214	3.439	3.617	3.77	3.903	4.020	4.125
$S_{restriction}^0$	-1.26	-1.25	-1.25	-0.94	-0.71	-0.54	-0.43	-0.34	-0.28	-0.23
Total	54.47	54.75	54.82	58.90	62.77	66.43	69.90	73.22	76.39	79.40
$-(G^0 - E_0^0)/T.$										
t.r.	44.275	44.464	44.513	46.810	48.597	50.023	51.249	52.310	53.246	54.084
vib.	0.106	0.118	0.121	0.400	0.852	1.456	2.149	2.923	3.762	4.625
free rot.	1.906	1.929	1.935	2.221	2.446	2.624	2.777	2.910	3.027	3.132
restrict.	-1.35	-1.34	-1.34	-1.26	-1.17	-1.07	-1.02	-0.93	-0.85	-0.79
Total	44.937	45.171	45.229	48.161	50.725	53.053	55.155	57.213	59.185	61.051
$(H^0 - E_0^0)/T.$										
t.r.	7.95	7.95	7.95	7.95	7.95	7.95	7.95	7.95	7.95	7.95
vib.	0.499	0.552	0.560	1.475	2.644	3.931	5.219	6.474	7.696	8.851
int. tors.	1.07	1.09	1.09	1.34	1.47	1.54	1.56	1.57	1.56	1.54
Total	9.52	9.59	9.60	10.76	12.06	13.42	14.73	15.99	17.21	18.34
$(H^0 - E_0^0).$										
Total kcal.	2.77	2.86	2.88	4.31	6.03	8.05	10.31	12.80	15.49	18.34
C_p^0										
t.r.	7.95	7.95	7.95	7.95	7.95	7.95	7.95	7.95	7.95	7.95
vib.	2.47	2.66	2.70	5.77	8.88	11.72	14.72	16.52	18.36	20.07
int. tors.	2.03	2.04	2.04	2.06	1.97	1.82	1.66	1.54	1.46	1.39
Total	12.45	12.65	12.69	15.78	18.80	21.49	24.33	26.01	27.77	29.41

(d) The reaction: $\text{CH}_4 + \text{HCN} \rightleftharpoons \text{CH}_3\text{CN} + \text{H}_2.$

From the heats of formation at 18° C., $-\Delta H = -6.94$ kcal., and at this temperature $\Delta(H^0 - E_0^0) = 0.27$, so that $\Delta E_0^0 = 6.67$ kcal. The free energy of H_2 is taken from Giauque's data, and Table IX gives the resulting equilibrium constants.

(e) The reaction: $\text{C}_2\text{H}_6 + \text{C}_2\text{N}_2 \rightleftharpoons 2\text{CH}_3\text{CN}.$

For calculations on this equilibrium the free energy function of C_2H_6 is needed. According to Frost,²⁸ the moments of inertia are

²⁷ J. Am. C.S., 1937, 59, 1264.

²⁸ Compt. rend. U.S.S.R., 1933, 161.

10.74 and 40.09×10^{-40} g. cm.², and the reduced moment of the two end methyl groups rotating about the C—C bond is 2.65×10^{-40} . With a staggered D_{3d} configuration, the symmetry number is 6. The vibrational spectrum has been studied by Crawford, Avery and Linnett,²⁹ and by Stitt,³⁰ and apart from the torsional mode the seventeen fundamentals are almost certainly: 827 (2), 993, 1170 (2), 1375, 1380, 1460 (2), 1465 (2), 2925 (2), 2960 (2), 2980 (2). Specific heat measurements have made it very probable that internal rotation about the C—C bond is restricted by a potential barrier of approximately 3000 cal.³¹ Assuming a twisting potential of the form $V = V_0 \cdot \sin^2 \sigma_1 \cdot \frac{\theta}{2} = \frac{1}{2} V_0 (1 - \cos \sigma_1 \theta)$,

with $\sigma_1 = 3$, the contributions of the torsional mode can be calculated from the tables of Pitzer.³² We thus obtain for the total translational plus rotational entropy at one atmosphere $S^0_{t.r.} = 4R \ln T + 7.122$. Table X summarises the remaining computations.

As before, taking the heats of formation at 18° C. from Bichowsky and Rossini, for reaction (e), $-\Delta H = 11.24$ kcal., and from the above tables $\Delta(H^0 - E_0^0) = -0.13$ kcal., so that $\Delta E_0^0 = -11.11$ kcal. Table XI summarises the remaining calculations.

TABLE XI.

°K.	$\Delta(G^0 - E_0^0)/T$.	$\Delta(G^0 - E_0^0)$.	ΔG^0 .	K_p .
300	-4.12	-1.24	-12.35	8.9×10^8
500	-3.79	-1.89	-13.0	4.4×10^6
600	-3.60	-2.16	-13.27	6.3×10^4
800	-3.48	-2.78	-13.89	5.9×10^3
1000	-3.45	-3.45	-14.56	1.4×10^3

(f) The reaction: $2C_2\text{graph.} + \text{NH}_3 \rightleftharpoons \text{CH}_3\text{CN}$.

Overstreet and Giauque³³ have found experimentally a third law entropy for NH_3 which is consistent with that calculated from moments

TABLE XII.—AMMONIA.

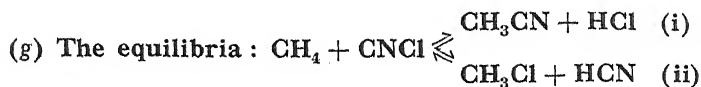
°K.	Entropy.			$-(G^0 - E_0^0)/T$.		$(H^0 - E_0^0)/T$ vib.	$(H^0 - E_0^0)$.	C_{vib} .	C^0_p .
	$S^0_{t.r.}$	$S_{vib.}$	$S_{tot.}$	Vib.	Total.				
291.16	45.70	0.119	45.82	0.020	37.773	0.098	2.34	0.50	8.45
298.16	45.89	0.130	46.02	0.022	37.964	0.108	2.41	0.54	8.49
300	45.94	0.134	46.07	0.023	38.015	0.111	2.42	0.55	8.50
400	48.23	0.382	48.61	0.080	40.362	0.302	3.30	1.22	9.17
500	50.02	0.737	50.76	0.173	42.245	0.563	4.25	2.19	10.14
600	51.45	1.172	52.62	0.316	43.818	0.856	5.28	2.71	10.66
700	52.67	1.636	54.31	0.458	45.180	1.178	6.39	3.43	11.38
800	53.74	2.154	55.89	0.636	46.428	1.518	7.58	4.11	12.06
900	54.67	2.656	57.33	0.832	47.554	1.823	8.79	4.76	12.71
1000	55.51	3.191	58.70	1.039	48.601	2.152	10.10	5.37	13.32

of inertia $I_1 = I_2 = 2.782 \times 10^{-40}$ and $I_3 = 4.33 \times 10^{-40}$, and vibration frequencies 948, 1631 (2), 3335, 3450 (2). The total translational

²⁹ *J. Chem. Physics*, 1938, 6, 686.³⁰ *Ibid.*, 1939, 7, 297.³¹ Kistiakowsky, Lacher and Stitt, *ibid.*, 289.³² *Ibid.*, 1937, 5, 469.³³ *J. Am. C.S.*, 1937, 59, 254.

plus rotational entropy is given by $S^0_{\text{t.r.}} = 4R \ln T + 0.60$. In Table XII values of the free energy are tabulated for different temperatures.

For the reaction (f) at 18° C., $-\Delta H = -30.84$ kcal., and $\Delta(H^0 - E_0^0) = -0.03$, so that $\Delta E_0^0 = 30.97$. The resulting values of ΔG_0^0 and K_p are given in Table XIII.



Stevenson³⁴ has calculated the free energy of CNCl, and Beach and Stevenson³⁵ that of CH_3Cl . Bichowsky and Rossini give the heat of formation at 18° C. of gaseous CNCl as -36.5 kcal. For reaction (g i) at 18° C. we then have $-\Delta H = 20.47$ kcal. and for (g ii) $-\Delta H = 7.66$ kcal. At the same temperature the values of $\Delta(H^0 - E_0^0)$ are 0.01 and -0.17 kcal. respectively, so that the values of ΔE_0^0 are -20.48 and -7.49 kcal. The equilibrium constants thus calculated

are collected in Table XIV. The free energy of HCl acid is taken from Giaque and Overstreet.

TABLE XIII.

°K.	ΔG_0^0	K_p
300	28.035	5×10^{-21}
500	26.175	4×10^{-12}
700	24.325	3×10^{-8}
1000	21.49	2×10^{-5}

TABLE XIV.

°K.	Reaction (g i).		Reaction (g ii).	
	ΔG_0^0	K_p	ΔG_0^0	K_p
300	-21.54	4×10^{15}	-9.22	4.8×10^6
500	-22.28	5×10^9	-10.17	2.6×10^4
700	-23.05	1.5×10^7	-11.14	2.9×10^3
1000	-24.34	2×10^5	-12.59	5.5×10^2

Summary.

The thermodynamic functions of methyl cyanide have been calculated statistically from the known moments of inertia and molecular vibration frequencies. Certain gaseous equilibria involving this substance have then been discussed. In the latter connection the thermodynamic functions of methane, ethylene, ethane, cyanogen, and ammonia have been calculated, using the most recent molecular data available.

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³⁴ J. Chem. Physics, 1939, 7, 171.

³⁵ Ibid., 1938, 6, 25, 108, 341.

THE POLAROGRAPHIC BEHAVIOUR OF HISTIDINE AND CERTAIN OTHER AMINO-ACIDS.*

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The principles of the Heyrovský-Shikata polarograph,¹ the instrument used in this investigation, are already well-known² and need no elaboration here.

Heyrovský and Babička³ observed that the current-voltage curves of albumins in deci-normal ammonium chloride solution exhibited two waves which were attributed to the catalytic deposition of hydrogen made possible by a weakening of the N—H bond from the complex $R \cdot NH_3-H^+$ ammonium-protein ion. A more striking effect⁴ was discovered in solutions of proteins buffered with ammonium chloride and ammonia and containing cobaltous ions; the cause of this effect, apparent only in sulphur-containing proteins, is the sulphhydryl group.⁴ This is the basis of Brdička's⁴ method for determining cystine.

Sladek and Lipschütz⁵ investigated a number of pure amino-acids, and reported cystine-like effects with phenyl-alanine and glutathione only; arginine, lysine and tryptophane provoked characteristic modifications of the current maximum which occurs when cobaltous ions are reduced to the metal. Histidine, however, suppressed this maximum but provoked a similar maximum at a more negative potential; since no deposition was observed, little importance was attached to this phenomenon.

The present research was undertaken to confirm previous work and to inquire more closely into the histidine effect.

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† Commonwealth Fund Fellow, University of Minnesota, 1938-40.

¹ Heyrovský and Shikata, *Rec. Trav. Chim. Pays-Bas*, 1925, 44, 496.

² Heyrovský, *Phil. Mag.*, 1923, 45, 303; *Rec. Trav. Chim. Pays-Bas*, 1925, 44, 488, 499; *Coll. Czech. Chem. Comm.*, XI, 1939, 98; *Actualités Scient. Industr.*, No. 90, 1934 (Herman et Cie, Paris); *Analyse, W. Böttger*, Teil II, 260 (Akad. Verlag, Leipzig) (1936). Emelianova and Heyrovský, *Trans. Faraday Soc.*, 1928, 24, 257. Heyrovský and Ilkovič, *Coll. Czech. Chem. Comm.*, VII, 1935, 198. Ilkovič, *Coll. Czech. Chem. Comm.*, VI, 1934, 498; VII, 1936, 13; *J. Chim. Physique*, 1938, 35, 129. Hohn, *Anleitung chem. Laboratoriumspraxis*, Bd. III (Springer, Berlin, 1937). Muller, *Chem. Reviews*, 1939, 24, 95. Antweiler, *Z. analyt. Chem.*, 1935, 102, 385; *Z. Electrochemie*, 1937, 43, 596; 1938, 44, 663. Lingane and Kolthoff, *J. Am. Chem. Soc.*, 1939, 61, 825, 1025; *Chem. Review*, 1939, 24, 1.

³ Heyrovský and Babička, *Coll. Czech. Chem. Comm.*, II, 1930, 370; *Chem. News*, 1930, 141, 369, 385.

⁴ Brdička, R., *Coll. Czech. Chem. Comm.*, V, 1933, 112, 148, 238; VIII, 1936, 366; *Mikrochemie*, 1934, 15, 167; *Biochem. Z.*, 1934, 272, 104.

⁵ Sladek and Lipschütz, *Coll. Czech. Chem. Comm.*, VI, 1934, 487.

Experimental.

The apparatus, a Heyrovský micropolarograph Type X, with its power supply unit Type II, and all its accoutrements, was first tested, using known solutions of inorganic salts. The results of these experiments were used in calibrating the machine.

The Basic Amino-acids : Histidine, Arginine and Lysine.

Solutions of these acids in concentrations varying from 10^{-5} to 10^{-2} M were electrolysed in the presence of 5×10^{-3} M cobaltous chloride,

10^{-1} N ammonia and 10^{-1} N ammonium chloride. In accordance with the results of Sladek and Lipschütz, lysine and arginine produced tremendous maxima at -1.05 volts, *i.e.* the potential at which cobaltous ions are reduced to the metal in ammoniacal solutions. In the case of histidine, however, this maximum was completely eliminated, giving place to a straightforward reduction curve, while at about -1.25 volts a second reduction wave occurred [(a) Fig. 1]. The current rapidly increases just beyond this point, rising to a sharp maximum at -1.55 volts [(b) Fig. 1] and then falls instantaneously to a value lower than the limiting current for the cobalt. Thereafter the current rises to a second, somewhat irregular maximum [(c) Fig. 1], falls again slightly, and finally increases very sharply as the ammonium ions are discharged. There are thus three distinct effects, (a), (b) and (c), on the current-voltage curve for histidine. Since the reduction wave is small, the maximum immediately following it was measured and its height found to be proportional to the concentration of histidine, provided that sufficient cobalt was present and that

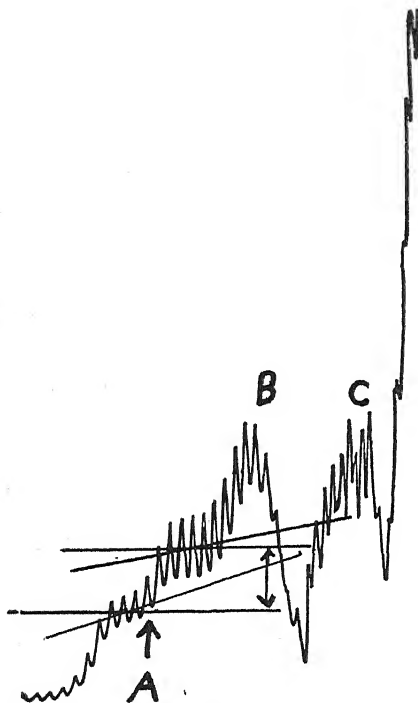


FIG. 1.—Polarographic wave of histidine. "A" at -1.25 volts, "B" at -1.55 volts, and "C" at still more negative voltage. The "A" wave is most proportional to histidine concentration.

the concentration of histidine lay between the limits 10^{-5} M and 10^{-4} M. The slope of the line when the height of the maximum in cm. was plotted against concentration of histidine was 0.27.

Effect of Arginine, Lysine and both on the Histidine Effects.

In view of the fact that the basic amino-acid fraction in protein analysis contains both arginine and lysine in addition to histidine, the effects of these acids, severally and jointly, on the histidine maximum was investigated. In all cases the histidine maximum at -1.55 volts was depressed. Preliminary experiments seemed to indicate that if the arginine and lysine concentrations were not too high, in fact not greater than half the histidine concentration, their depressing effect was very small.

It appeared possible, therefore, that histidine in such a mixture might be estimated by adding known amounts of pure histidine until the maximum began to behave exactly as a pure histidine solution. Many experiments conducted along these lines, however, proved that this was not possible, for although there was a strict proportionality between the height of the maximum and histidine concentration, the proportionality factor was influenced by the presence of the other basic amino-acids. Moreover, the range of histidine concentration over which this proportionality holds was found to differ according to the concentrations of arginine and histidine. It is apparent, then, that this effect persists so long as arginine and lysine do not predominate too heavily.

A series of experiments, designed to eliminate arginine as the di-flavianate and to remove the excess of flavianic acid by precipitation as the barium salt, was unsuccessful. Flavianic acid itself is reduced at a much more positive cathode potential than that at which the histidine maximum appears, and, unfortunately, the latter is exalted. If it were possible always to have exactly the same concentration of flavianic acid in the solution, this exaltation should be a constant, determinable error, but this condition was never attained; in spite of great care in obtaining the barium precipitate, this latter was always slightly different in appearance and behaviour.

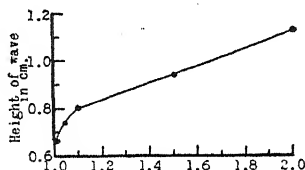


FIG. 2.—Showing height of the polarographic "A" wave in relation to histidine concentration.

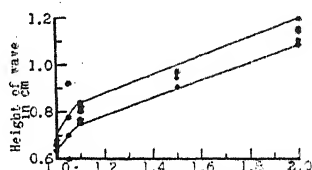


FIG. 3.—Showing variability of "A" wave height for different replicates of identical solutions. (The region between the upper and lower curves indicates the experimental variability in height which may be expected.)

In view of the fact that, judging from the above experiments, it would be difficult to estimate histidine unless a large volume of empirical data had been accumulated, it was decided to attack the problem from a slightly different angle. A large number of solutions, containing different amounts of histidine, arginine and lysine, and identical amounts of cobaltous chloride and ammonium chloride-ammonia buffer solution, were subjected to electrolysis and on this occasion the first reduction wave (*a*) was measured. Since this reduction wave is completely "inside" the maximum provoked by arginine and for lysine, it was necessary to eliminate this maximum. This, however, proved very difficult. Of the many substances which are known to suppress maxima, starch and, to a smaller extent, thorium only were sufficiently effective; unfortunately, however, starch eliminates the histidine maximum also, and apparently diminishes the reduction wave. The only really effective way to remove the troublesome maximum is to add sufficient histidine to the solution. When this fact was recognised, only solutions 1 to 2×10^{-3} M with respect to histidine were electrolysed. These solutions were 10^{-5} to 10^{-3} M with respect to lysine, and 10^{-4} to 10^{-2} M with respect to arginine.

While the histidine maximum in solutions of identical histidine concentration, but of different arginine and lysine concentrations, showed some variation, the small reduction wave was found to be much more constant, especially in the solutions rich in histidine. A curious fact was observed when the reduction step was plotted against concentration

of histidine. The slope of this curve, Fig. 2, shows a sharp break at about 1.10×10^{-3} M. Between 1×10^{-3} M and 1.10×10^{-3} M, the slope is quite steep and the line practically straight. Between 1.10×10^{-3} M and 2.0×10^{-3} M, the curve, while still straight, has a much smaller gradient.

The significant fact is that the current step appears to be independent of the presence of arginine and lysine, since the variations obtained were no greater than those obtained when the same solution was electrolysed in quadruplicate. Thus provided we have a sufficient concentration of histidine to suppress completely the maxima caused by arginine and lysine, the solution can be analysed polarographically directly for histidine in spite of the presence of arginine and lysine.

Data from several series of experiments are shown in Table I.

TABLE I.—THE POLAROGRAPHIC ESTIMATION OF HISTIDINE IN THE PRESENCE OF ARGININE AND LYSINE.

Expt. No.	Lysine Conc. Molarity $\times 10^4$.	Arginine Conc. Molarity $\times 10^4$.	Histidine Conc. Molarity $\times 10^4$.	Height of Reduction Wave "A", cm.*	
4	1	10	50	0.48	
5	1	10	100	0.94	
9	1	50	60	0.62	
10	1	50	110	0.84	
15	1	100	200	0.75	
30	5	10	110	(0.47)	(Soln. cont. starch)
31	5	50	101	0.66	(0.50)
32	5	50	105	0.60	(0.38)
33	5	50	110	0.80	(0.57)
34	5	50	150	0.90	
35	5	50	200	1.15	(1.02)
36	5	100	101	0.68	(0.60)
37	5	100	105	0.92	(0.60)
38	5	100	110	0.77	(0.65)
39	5	100	150	0.96	(0.82)
40	1	100	200	1.14	(0.89)
51	10	10	101	0.68	
52	10	10	105	0.77	
53	10	10	110	0.75	
54	10	10	150	0.84	
55	10	10	200	1.08	
56	10	50	101	0.81	
57	10	50	105	0.70	
58	10	50	110	0.82	
59	10	50	150	0.94	
60	10	50	200	1.10	
61	10	100	101	0.62	
63	10	100	110	0.94	
64	10	100	150	0.97	
65	10	100	200	1.19	

SUMMARY.

Histidine Conc. $\times 10^3$ M.	Mean Wave cm.
1.01	0.66
1.05	0.74
1.10	0.80
1.50	0.94
2.00	1.13

* Mean of four measurements.

Cystine.—A few experiments were made with cystine, using solutions 10^{-5} M with respect to cystine and containing cobaltous chloride buffered with ammonium chloride and ammonia. These were found to give reproducible values for cystine only if polarograms were made within a short time of preparing the solution. It appears, however, that if the ammonia is omitted, the solution may stand indefinitely; if ammonia is added immediately prior to electrolysis, the results are identical with those

obtained with an entirely freshly prepared solution. If the complete solution is allowed to stand, the cystine content appears to decrease until, at the end of about five days, virtually none remains.

Serine.—In view of the structural resemblance between serine and cystine, experiments were made with serine in the usual buffered cobalt solutions. Serine, however, appears to be polarographically inactive under these conditions; neither is this amino-acid reduced in lithium chloride solution.

Tryptophane, Tyrosine and Phenylalanine.—These amino-acids were subjected to cursory examination and the results of Sladek and Lipschütz confirmed.

Discussion.

While accepting the general catalytic theory of Brdička to explain the sulphhydryl group reaction, and believing that a similar scheme, involving one of the imidazole nitrogen atoms (instead of sulphur) might to some extent account for the behaviour of histidine, the author finds it difficult to relate to any present theory of polarography the fact that after attainment of the maximum, the histidine curve drops to a current value *less* than that of the cobalt diffusion current. This phenomenon was observed consistently in the foregoing experiments. Assuming that it is a real effect—this could not be checked by reversing the curve, since the instrument used had no provision for applying a decreasing potential—it is suggested that the various resonance forms of histidine⁶ may be differently distributed under different electric fields such as are experienced in the immediate neighbourhood of the mercury drop.

With regard to the general shape of the histidine polarogram, there are indications of a reduction, followed by a catalytic deposition of hydrogen. Then comes the remarkable decrease in the current and finally an irregular maximum somewhat irreproducible in detail but quite definite which appears to be a further deposition of hydrogen.

Summary.

1. Histidine, when analysed polarographically, exhibits three characteristic effects, two of which, under specific conditions, are proportional to the concentration of histidine. One of these effects persists and retains proportionality in presence of arginine and lysine. This "wave" may be utilised for analytical purposes.

2. Cystine determinations must be made on freshly prepared solutions.

3. Serine, tryptophane and tyrosine do not lend themselves to polarographic estimation.

The author wishes to express his gratitude to Professor Ross Aiken Gortner for his enthusiastic interest in the above research.

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⁶ Hill and Branch, *Science*, 1940, 91, 145.

THE CONSTANTS OF THE BEATTIE-BRIDGEMAN EQUATION.

BY J. CORNER.

Received 14th May, 1941.

Theoretical work on the properties of gases has been mainly devoted to equations of state of the type :

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots \quad (1)$$

where P , V , and T are the pressure, volume and temperature of a mole of gas ; R is the gas-constant ; B , C , ... are functions of the temperature called the second, third and higher virial coefficients. Among empirical equations of state, the Beattie-Bridgeman¹ form is probably the most widely used. This equation is

$$PV^2 = RT \left(1 - \frac{c}{VT^3} \right) \left(V + B_0 - \frac{bB_0}{V} \right) - A_0 \left(1 - \frac{a}{V} \right) \quad (2)$$

where A_0 , B_0 , a , b , c are five empirical constants, depending only on the nature of the gas. Although Beattie and Bridgeman attempted a theoretical justification of their equation, it has usually been regarded as purely empirical. Recently Hirschfelder and Roseveare² have interpreted the constants A_0 , B_0 and c in terms of intermolecular forces, by comparing the second virial coefficient of (2) with that calculated from intermolecular forces by Lennard-Jones.³ In this note we wish to point out that a and b can be derived in a similar way by investigating the third virial coefficient. The essential step, namely, the calculation of theoretical third virial coefficients, has been carried out by de Boer and Michels.⁴

The intermolecular potential is assumed to be

$$12\phi_0 \left\{ \frac{1}{12} \left(\frac{r_0}{r} \right)^{12} - \frac{1}{6} \left(\frac{r_0}{r} \right)^6 \right\} \quad (3)$$

This has been successful in accounting for the second virial coefficients of the simpler gases.³ The depth of the potential is ϕ_0 ; (Hirschfelder and Roseveare call this E_0). The minimum of the potential occurs at $r = r_0$. The potential is zero at $r = 2^{-1/6}r_0$, which is the r_0 of Hirschfelder and Roseveare and the σ of de Boer and Michels. There are only two adjustable constants in the potential, so that all gases with such potentials will obey the law of corresponding states, if the motion of the molecules can be treated classically. In particular there will be really only two arbitrary constants in the Beattie-Bridgeman equation ; a , b , c will be derivable from A_0 and B_0 . Now in practice the law of corresponding states is obeyed only roughly, so we must expect at best

¹ Beattie and Bridgeman, *Proc. Amer. Acad. Sci.*, 1928, **63**, 229.

² Hirschfelder and Roseveare, *J. Physic. Chem.*, 1939, **43**, 15.

³ The work is described in Fowler, *Statistical Mechanics*, ch. X.

⁴ de Boer and Michels, *Physica*, 1939, **6**, 97.

a rough agreement with average results. We will shew that the potential (3) does predict relations for a and b which agree with the experimental results to within their rather considerable fluctuations from gas to gas. This shows that (3) is a fairly satisfactory form for a two-constant potential. To get agreement with the results on individual gases it would be necessary to introduce at least one more arbitrary parameter into the intermolecular potential.

By fitting the second virial coefficient of (2) to the values derived theoretically by Lennard-Jones from (3), Hirschfelder and Roseveare showed that

$$\phi_0 = 4.127 \times 10^{-17} \frac{A_0}{RB_0} \text{ ergs} \quad . \quad . \quad . \quad (4)$$

$$b_0 = \frac{\sqrt{2\pi N} r_0^3}{3} = 1.249 B_0 \quad . \quad . \quad . \quad (5)$$

where N is Avogadro's number. These equations interpret A_0 and B_0 .

Also
$$c = 0.0236 \frac{A_0^3}{R^3 B_0^2} \quad . \quad . \quad . \quad (6)$$

This is a test of the validity of (3). The agreement is good for Ne, A, N₂ and CO; it is fair for H₂, O₂, CO₂, NO and CH₄. As a matter of fact, equation (6) is a severe test of (3). We have repeated the process for a potential

$$18\phi_0 \left\{ \frac{1}{9} \left(\frac{r_0}{r} \right)^9 - \frac{1}{6} \left(\frac{r_0}{r} \right)^6 \right\} \quad . \quad . \quad . \quad (7)$$

in which ϕ_0 and r_0 have the same physical meanings as before. The change, from 12 to 9, in the index of the repulsive part of the potential, leads to these equations, which replace (4), (5) and (6)

$$\phi_0 = 3.104 \times 10^{-17} \frac{A_0}{RB_0} \text{ ergs} \quad . \quad . \quad . \quad (8)$$

$$\frac{\sqrt{2\pi N} r_0^3}{3} = 1.367 B_0 \quad . \quad . \quad . \quad (9)$$

$$c = 0.0128 \frac{A_0^3}{R^3 B_0^2} \quad . \quad . \quad . \quad (10)$$

There is a considerable difference between (6) and (10). All the cases listed by Hirschfelder and Roseveare as "fair agreement" would become good agreement by changes of this order in the constant of (6), that is, by suitable changes of two or three units in the index of the repulsive term.

By expanding (2) in powers of $1/V$, the third virial coefficient of the Beattie-Bridgeman equation is found to be

$$C = \frac{aA_0}{RT} - \frac{cB_0}{T^3} - bB_0 \quad . \quad . \quad . \quad (11)$$

We introduce the non-dimensional variable $\tau = kT/\phi_0$, and use the relations (4), (5) and (6). The result is

$$C = \left(\frac{\sqrt{2\pi N} r_0^3}{3} \right)^2 \left[-0.641 \frac{b}{B_0} + 2.129 \frac{a}{B_0} \cdot \frac{1}{\tau} - \frac{0.555}{\tau^3} \right] \quad . \quad (12)$$

de Boer and Michels ⁴ have recently calculated the third virial coefficient, using the intermolecular potential (3). Their results cover the range of τ from 4 to 1.5, which correspond to temperatures about 3 and 1.1 times the critical temperature. They tabulate C^* , defined by

$$C = \left(\frac{\sqrt{2\pi} N r_0^3}{3} \right)^2 C^* \quad (13)$$

If then we represent $C^* + 0.555/\tau^3$ by a linear function of $1/\tau$, we obtain theoretical estimates of a/B_0 and b/B_0 . These are found to be

$$a/B_0 = 0.445; \quad b/B_0 = -0.098. \quad (14)$$

The corresponding linear function, which was obtained by a least-squares method, fits the calculated values of $C^* + 0.555/\tau^3$, with errors up to 7 %.

The experimental values ¹ are given in Table I. We include helium because it seems to indicate why neon has such a high value of a/B_0 . Quantum effects must be important for light molecules such as helium,

TABLE I.—THEORETICAL AND OBSERVED VALUES OF a/B_0 AND b/B_0 .

Gas.	a/B_0 .	b/B_0 .	Agreement in Case of (6).
He	4.17	0	Poor
Ne	1.07	0	Good
A	0.59	0	"
N ₂ (and also CO)	0.52	-0.1	"
H ₂	-0.24	-2.1	Fair
O ₂	0.55	0.1	"
CO ₂	0.68	0.7	"
CH ₄	0.33	-0.3	"
Theoretical .	0.45	-0.1	

and are probably appreciable for neon. The negative value of a/B_0 for hydrogen is considered by Beattie and Bridgeman to be due to a slight trend in the experimental results; by comparison with helium a high value of a/B_0 would be expected.

There is fair agreement for the gases with simple molecules, such as A, N₂, CO, O₂, CH₄. This agreement is as good as can be expected from any potential with only two constants. It seems likely that the variations from gas to gas could be represented by small variations in the index of the intermolecular repulsion. At present the third virial has been calculated for only one such index, 12.

There is, however, a limit to the accuracy with which a and b can be derived from the experimental data. Small changes in the compressibility data to which the Beattie-Bridgeman equation is fitted, may require changes in all the constants, and especially of b . Deming and Shupe ⁵ have given a set of constants for nitrogen, which lead to $a/B_0 = 0.41$; $b/B_0 = -0.6$, compared with the 0.52 and -0.1, respectively, of Beattie and Bridgeman. Therefore it seems unwise to discuss the constants a and b , except as regards their orders of magnitude; these are certainly in agreement with the theoretical third virial coefficient.

Maron and Turnbull ⁶ have arrived at certain results which can be

⁵ Deming and Shupe, *J. Am. Chem. Soc.*, 1930, **52**, 1382.

⁶ Maron and Turnbull, *Indust. Eng. Chem.*, 1941, **33**, 69, 246, 408.

correlated with those which we have quoted. Their method of approach made no explicit use of intermolecular forces. They found an approximate activity coefficient for the gas, depending on its pressure, temperature, and the five constants of the Beattie-Bridgeman equation. Now it is known that the activity coefficients of all gases can be closely represented by a single function of the reduced temperature and pressure. This condition requires that the Beattie-Bridgeman constants shall be of the form

$$A_0 \propto T_c^2/P_c; B_0 \propto T_c/P_c; c \propto T_c^4/P_c; a \propto T_c/P_c; b \propto T_c/P_c \quad (15)$$

where the coefficients of proportionality are the same for all gases. Maron and Turnbull found the coefficients from the known constants of nitrogen.

These results can be converted into the results given earlier in this note, by using known relations between the intermolecular force constants and the critical temperature and pressure. For example, ϕ_0/T_c and b_0/V_c (or b_0P_c/T_c) are roughly constant for all gases (b_0 is defined in (5)). The first of these, and (15), reproduce (4) except for the numerical constant. The second, and (15), lead to (5). Equation (6) is a direct consequence of (15). Also the statement embodied in (14) and Table I that a/B_0 and b/B_0 are the same for all gases, is seen to be included in (15). The connection between the two approaches is simple: the intermolecular potential used has only two parameters, of the dimensions of energy and length, and all the derived results necessarily obey the law of corresponding states; Maron and Turnbull have started from this law. The numerical constants can be evaluated from the assumed form of intermolecular potential or, as Maron and Turnbull do, from a standard gas.

Summary.

It is shown that the third virial coefficients calculated by de Boer and Michels can be used to interpret the constants a and b of the Beattie-Bridgeman equation.

I am indebted to Professor J. E. Lennard-Jones for his interest in this work.

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ETHYLENE AND ACETYLENE ADSORPTION IN HYDROGENATION CATALYSIS.

By E. F. G. HERINGTON.

Received 20th May, 1941.

In catalytic hydrogenation of unsaturated hydrocarbons at metallic surfaces, *e.g.*, Ni or Co, there is much evidence for the assumption that the chemisorption of the hydrocarbon is an important factor, one of the most convincing being the cessation of the *para* hydrogen conversion during the hydrogenation of ethylene.¹ One of the earlier attempts to

¹ Farkas, Farkas and Rideal, *Proc. Roy. Soc.*, 1934, **146**, 630.

depict the structure of such a chemisorbed complex was that of Balandin,² who postulated in benzene that the ring lay plane to a crystal facet of the nickel surface. This conception, somewhat artificial in character, does not appear to have been developed. More recently Sherman, Sun and Eyring³ have calculated the activation energy of the reaction benzene to dihydrobenzene. The mode of adsorption was not specifically discussed, although the adsorbed benzene complex is represented as in Fig. 1.

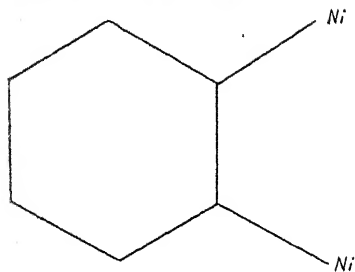


FIG. 1.

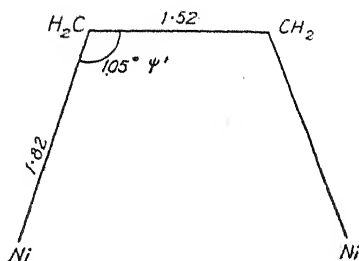


FIG. 2.

In a recent paper, Twigg and Rideal⁴ demonstrated that ethylene could be adsorbed on nickel atoms spaced at their distance of closest packing in the crystal surfaces, *viz.*, 2.47 Å. Taking the distances C—Ni = 1.82 Å., C—C = 1.52 Å. (Fig. 2), the angle subtended was found to be 105° 4' in lieu of the tetrahedral angle of 109° 28'. The formation of the complex would thus be effected, involving either a very small distortion or a slight twist so that the C—C axis lies at a small angle to and not parallel to the Ni—Ni axis. Recently Beeck, Smith and Wheeler⁵ have demonstrated

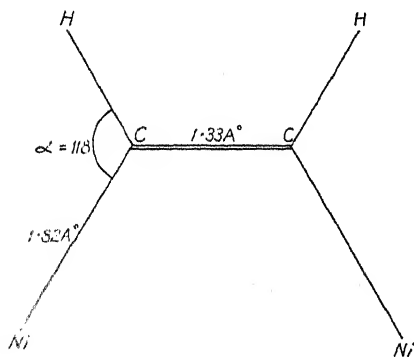


FIG. 3.

in an elegant manner the catalytic activity of the 110 plane of nickel for ethylene hydrogenation. They attribute the activity, however, to the supposed ease with which the chemisorption of hydrogen can occur on the long spacing 3.5 Å. which is also present in this plane (110). We have noted the arguments in favour of the supposition that the chemisorption of the olefine rather than of the hydrogen is required. This is supported by an examination of the chemisorption of acetylene

and its reactivity, and the steps involved in the Fischer Tropsch synthesis.

We may note in passing that the spacing characteristics of Co are very similar to those of Ni, thus in the face centred α crystals the side

² Balandin, *Z. physik. Chem.*, B (2), 1929, 289.

³ Sherman, Sun and Eyring, *J. Chem. Physics*, 1935, 3, 49.

⁴ Twigg and Rideal, *Trans. Faraday Soc.*, 1940, 36, 533.

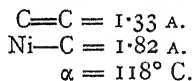
⁵ Beeck, Smith and Wheeler, *Proc. Roy. Soc.*, 1940, 177, 62.

⁶ Ewens and Lister, *Trans. Faraday Soc.*, 1939, 35, 681. See also Brockway and Anderson, *ibid.*, 1937, 33, 1233.

is 3.55 Å. The Co—C distance from cobalt carbonyl derivatives is 1.83 ± 0.02 Å.⁶

We may depict the adsorption of acetylene on Ni or Co as follows:—

Taking the following bond lengths for ethylene



(See Penney⁷ and also Thompson⁸) we obtain as a calculated distance for the Ni—Ni

$$1.33 - 2 \times 1.82 \cos 121 = 3.20 \text{ Å.}$$

compared with the normal distance of 3.50 Å. for the side of the face-centred cube.

However, interaction between the nickel and hydrogen will probably tend to decrease the NiCH angle below 118° . If the normal tetrahedral angle $109^\circ 28'$ be taken for α , the Ni—Ni distance will be

$$1.33 - 2 \times 1.82 \cos 125^\circ 16' = 3.43 \text{ Å.}$$

Ethylene and acetylene are thus most readily adsorbed by two-point contact on different Ni spacings. In Table I are given the distribution of the two distances on the three common faces, the 100, 110 and 111 planes respectively; the results are expressed as the reciprocal of the number of bonds per square Ångström. Small areas thus indicate a high surface concentration.

TABLE I.

Face.	Area Å ² containing One Spacing 2.47 Å.	Area Å ² containing One Spacing 3.50 Å.
111	1.76	Nil
110	8.65	8.65
100	3.07	6.05

The 111 face should thus be incapable of chemisorbing acetylene; the 110 should adsorb both gases equally, and the 100 face should adsorb ethylene and acetylene in the ratio 2 : 1.

Twigg and Rideal⁴ showed that the 110 plane could be completely covered with ethylene. It is of interest to repeat this calculation for the case of acetylene.

Using the following values,

$$\begin{aligned}\text{C}-\text{H} \text{ bond} &= 1.09 \text{ Å.} \\ \text{Radius of hydrogen atom} &= 0.78 \text{ Å.} \\ \text{H} \hat{\text{C}} \text{H} &= 109^\circ 28' .\end{aligned}$$

The distances x and y shown in Fig. 4a which depicts the elevation of adsorbed acetylene molecule, can be calculated. These values may then be used to draw the plan given in Fig. 4b.

$$\begin{aligned}x &= \text{C}-\text{H} \cos 55^\circ 44' = 0.63, \\ y &= \text{Ni}-\text{C} \cos 55^\circ 44' = 1.05.\end{aligned}$$

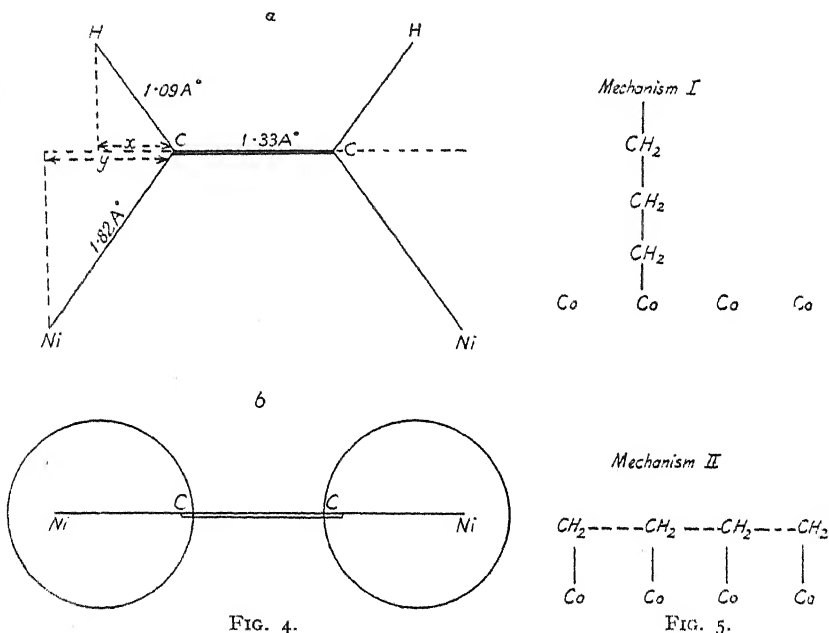
⁷ Penney, *Proc. Roy. Soc., A*, 1937, 158, 306.

⁸ Thompson, *Trans. Faraday Soc.*, 1939, 35, 697.

From this plan it follows that acetylene may completely cover the 110 face, partially cover the 100 plane and will not be adsorbed on the 111 face.

According to the above hypothesis, adsorbed C_2H_4 has no free valencies, while C_2H_2 is potentially reactive. This is in agreement with experience. Acetylene will polymerise in the presence of H_2 and a Co catalyst, while C_2H_4 is merely hydrogenated to C_2H_6 .

In a previous communication from this laboratory, investigations on the mechanism of the Fischer Tropsch synthesis were described,⁹ and arguments were advanced for the hypothesis that the stages in the synthesis involved the polymerisation of CH_2 groups formed by a series of steps from chemisorbed CO. Two different mechanisms have been



advanced for this process of linking of the CH_2 -groups which are depicted in the following diagrams.

According to Mechanism I, the chain of CH_2 groups grows by a further combination with the terminal CH_2 group in contact with the catalyst. On this view the CH_2 groups must be mobile on the surface and the desorbed olefine must be an $\alpha\beta$ mono olefine. According to Mechanism II the adsorbed CH_2 groups are regarded as portions of giant molecules from which fragments may be broken off. We have seen, however, that on Ni and Co the atomic spacings are such that two-point contact of an olefine can be maintained and thus the probable mechanism for the Fischer Tropsch synthesis would appear to be as in Fig. 6.

Two of the CH_2 groups produced by the reduction of carbide condense to form C_2H_4 which in its turn reacts with an adjacent CH_2 group to yield C_3H_6 . Simultaneously the migration of a H atom occurs and

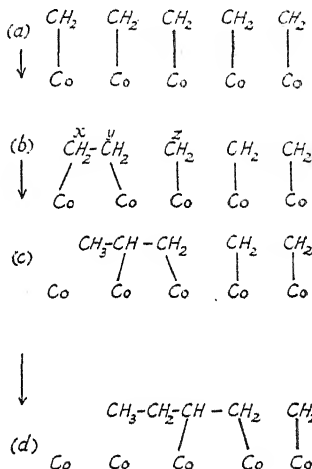
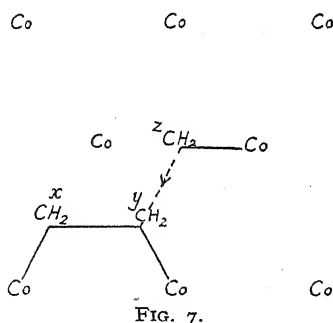
⁹ Craxford, *Trans. Faraday Soc.*, 1939, **35**, 946.

two-point contact is maintained. If the CH_2 groups were arranged linearly the distance between y and z would be too great for interaction, and in reality the atoms x , y and z in the basal plane are as shown in Fig. 7, which is a projection on to the plane of the catalyst.

On this mechanism a ready interpretation is given for the occurrence of a mono-olefine with the double bond in the terminal position as a primary product, and in addition indicates the unique position of C_2H_4 , since this is the only hydrocarbon to be held by all its C atoms and also possess two reactive centres for further polymerisation. Consequently the yield of C_3H_4 (and C_2H_6) is less than for higher homologues.

Evidence in support of these conceptions is also found in a comparison of the products obtained by incorporating C_2H_4 or C_2H_2 in the mixture of CO and H_2 used for the Fischer-Tropsch synthesis. The behaviour of these two substances should be very different, for while C_2H_4 is adsorbed on the same short spacing as is normally in use for the oil synthesis, C_2H_2 is held on the larger (3.50 Å.) spacing. Ethylene, therefore, should take part in the normal hydrocarbon synthesis, while C_2H_2 should be without influence on the $\text{CO} + \text{H}_2$ reaction although the C_2H_2 should continue to polymerise as it normally does in the presence of H_2 and a Co catalyst. These anticipations are fulfilled.

Ethylene is incorporated in the oil products and in addition yields liquids containing O (see Smith, Hawk and Golden¹⁰). On the other hand, in experiments at the Fuel Research Station of the Department of Scientific and Industrial Research it was found that the products from a mixture of C_2H_2 , CO and H_2 are indistinguishable from a



mixture of the C_2H_2 plus H_2 and CO plus hydrogen products and do not contain appreciable quantities of oxygen-containing compounds.

Summary.

The spatial conditions for the chemisorption of acetylene and ethylene on the crystal facets of Ni and CO are compared and it is shown that whilst C_2H_4 should be held on the short spacing 2.47 Å., C_2H_2 will be held on the long 3.50 Å. Support for these views is found in the different behaviour of these gases in the Fischer-Tropsch synthesis.

¹⁰ Smith, Hawk and Golden, *J.A.C.S.*, 1930, 52, 3221.

The considerations dealt with in this paper arose out of an investigation of problems of catalysis which is being carried out by the author in the Department of Colloid Science, Cambridge, and forms part of the Fuel Research programme of the Department of Scientific and Industrial Research. The Paper is published by permission of the Director of Fuel Research.

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The author wishes to thank Professor Rideal for his encouragement and assistance.

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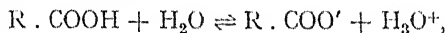
THE TEMPERATURE DEPENDENCE OF THE IONISATION CONSTANTS OF MONOCARBOXYLIC ACIDS.

BY J. F. J. DIPPY AND H. O. JENKINS.

Received 4th November, 1940.

Very few data relating to the variation of ionisation constants with temperature are available, and those of a reliable character are still further limited. Apart from the precision work of American investigators^{1, 2, 3} certain early conductimetric measurements⁴ cover in some cases a wide range of temperature, but thermodynamic considerations did not enter into these investigations, which fact, coupled with the use of the old, unrefined technique, renders them unsuitable for quantitative interpretation.

Nevertheless there is good reason to believe that a real relation exists between the ionisation constant (K), and temperature (T), and, for dissociations of the type



it is known that K passes through a maximum. The attempts to arrive at a precise equation, however, were attended only with partial success, to judge from the diverse conclusions reached so far.

¹ (a) Harned and Ehlers, *J. Am. Chem. Soc.*, 1933, **55**, 652, 2377; (b) Harned and Embree, *ibid.*, 1934, **56**, 1042; (c) Harned and Sutherland, *ibid.*, 1934, **56**, 2039; (d) Wright, *ibid.*, 1934, **56**, 314; (e) Nims and Smith, *J. Biol. Chem.*, 1936, **113**, 145; (f) Nims, *J. Amer. Chem. Soc.*, 1936, **58**, 987; (g) Hamer, Burton and Acree, *Bur. Standards J. Research*, 1940, **24**, 267 (second dissociation constant of malonic acid).

² (a) Harned and Embree, *J. Am. Chem. Soc.*, 1935, **57**, 1669; (b) Harned and Kazanjian, *ibid.*, 1936, **58**, 1912; (c) Harned and Fallon, *ibid.*, 1939, **61**, 2377.

³ (a) Martin and Tartar, *ibid.*, 1939, **59**, 2672; (b) Brescia, LaMer and Nachod, *ibid.*, 1940, **62**, 614 (92.5 % deuterioacetic acid).

⁴ (a) Arrhenius, *Z. physik. Chem.*, 1889, **4**, 96; (b) Jahn, *ibid.*, 1895, **16**, 72; (c) Wood, *ibid.*, 1895, **18**, 521; (d) Euler, *ibid.*, 1896, **21**, 257; (e) Schaller, *ibid.*, 1898, **25**, 497; (f) H. C. Jones, *Publ. Carnegie Inst. Washington*, 1912, **170**.

1. Harned's Equations.

These efforts have been due to Harned and co-workers,^{1a, 5, 6} Pitzer,⁷ and Everett and Wynne-Jones,⁸ while Gurney⁹ and Baughan¹⁰ have sought to give the relationships theoretical support.

In the earlier systematisation of their experimental results, Harned and collaborators^{1a} used a four-constant equation of the form

$$\log K = -a/T + b \log T + cT + d \quad . \quad . \quad (1)$$

whereas later Harned and Embree⁵ proposed the equation,

$$\log K = \log K_m - 5.0 \times 10^{-5} (t - \theta)^2 \quad . \quad . \quad (2)$$

where K_m is the maximum value of the ionisation constant, and θ the corresponding temperature in °C. Calculation shows that with acetic acid, for example, divergent values (-33.91 and -41.3) are derived for $(\Delta C_p)_{25}$ according to whether equation 1 or equation 2 is employed. In view of this it seems clear that when data are fitted to equations involving three or four constants, even though the results are co-ordinated satisfactorily in the experimental range, no absolute significance can be attached to the "constants," even in the range of experiment and certainly not outside it.

2. The Equations of Pitzer and Everett and Wynne-Jones.

Pitzer⁷ has put forward the equation

$$\ln K = \frac{A}{T} + \frac{\Delta C_p \ln T}{R} + B \quad . \quad . \quad (3)$$

and assuming a constant value of $\Delta C_p = -40$ cal./deg. for the ionisation of the fatty acids, invariant also with respect to temperature, he claims that his equation represents the data better than does the empirical equation of Harned and Embree.

Later, Everett and Wynne-Jones⁸ still keeping the invariance of ΔC_p with respect to temperature, but allowing a variation from acid to acid (such variation being determined by the experimental data), arrived at the equation,

$$\ln K = -\frac{\Delta H_0}{RT} + \frac{\Delta C_p \ln T}{T} + \frac{(\Delta S_0^\circ - \Delta C_p)}{R} \quad . \quad . \quad (4)$$

This contains three constants, ΔH_0 , ΔS_0° and ΔC_p , which are held to be unaffected by temperature (the first two presumably unaffected also by solvent), and it was contended that this equation is superior to any of the others previously advanced.

In an earlier paper Wynne-Jones¹¹ discussed the influence of solvent upon ionisation constant. He derived theoretically, from the Born equation,¹² a linear relation between $\log K$ and $1/D$ (D being the di-

⁵ Harned and Embree, *J. Am. Chem. Soc.*, 1934, **56**, 1050.

⁶ Harned and Owen, *Chem. Reviews*, 1939, **25**, 31.

⁷ Pitzer, *J. Am. Chem. Soc.*, 1937, **59**, 2365.

⁸ Everett and Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35**, 1380.

⁹ Gurney, *J. Chem. Physics*, 1938, **6**, 499.

¹⁰ Baughan, *ibid.*, 1939, **7**, 951; see also LaMer and Brescia, *J. Am. Chem. Soc.*, 1940, **62**, 617.

¹¹ Wynne-Jones, *Proc. Roy. Soc.*, 1933, **140**, 440.

¹² Born, *Z. Physik*, 1920, **1**, 45.

electric constant of the medium), which he tested by means of data relating to acids in aqueous, methyl alcoholic and ethyl alcoholic solutions at 25° C. It is significant that these measurements refer to a *fixed* temperature, and yet an attempt has now been made to question the use of such data even for qualitative purposes. The bridging of this apparent divergence of opinion is not made clear, but harmony should not be altogether impossible.

Equation 4 does contain a term ΔC_p which depends on the dielectric constant, as shown by the data of Harned and Embree^{2a} and Harned and Kazajian.^{2b} The form of the dependence may be uncertain, as few data are available for testing, but it would appear as though a linear relation,

$$\Delta C_p = x - yD, \quad (5)$$

holds for acetic acid in water-dioxane mixtures, x and y being constants. Nevertheless, the reconciliation of equation 4 with the $\log K - 1/D$ relation also necessitates a knowledge of how the dielectric constant varies with temperature. Consideration is given to this variation by Everett and Wynne-Jones in connection with the possibility of using the Born equation to provide reasonable values of ΔC_p in ionisation processes. Combining this equation with the usual thermodynamic relationships, we have

$$\Delta C_p = -\frac{z^2 e^2}{r} T \frac{\partial^2}{\partial T^2} \left(\frac{1}{D} \right) \quad (6)$$

where r is a mean ionic radius. Evaluation of $\frac{\partial^2}{\partial T^2} \left(\frac{1}{D} \right)$ in equation 6 obviously requires a knowledge of the dielectric constant-temperature law, and in this connection equation 7 finally commended itself to the above authors, since it provides for an almost temperature invariant ΔC_p , in conformity with initial hypothesis

$$\log D = A - B \log T. \quad (7)$$

TABLE I.

$T(^{\circ}\text{K})$.	$D_{\text{calc.}}$	$D_{\text{obs.}}$
$\frac{1}{D} = -0.00546 + 0.0000613T$		
273	88.65	88.31
293	79.95	80.35
313	72.83	73.12
333	66.88	66.62

This led to a calculated value of ΔC_p of about -10 cal./deg. at 25° C., leaving a considerable residue to be accounted for otherwise. A freezing out of water molecules in the co-ordination shell of the ions was accordingly postulated, a process which results in the loss of translational degrees of freedom and changes in the specific heat accompanying ionisation.

It can be shown, however, that other equations will account for the temperature variation of the dielectric constant of a liquid such as water; we may suggest

$$\frac{D-1}{D+2} = a - b \log T \quad (8)$$

and

$$\frac{1}{D} = a + bT. \quad (9)$$

The suitability of equation 9 for water is illustrated by Table I. In addition, the following equation (10) can also be suggested; this bears

a resemblance to the equation recently advanced by Onsager¹³ to account for the dielectric properties of polar liquids

$$\frac{(D-1)(2D+1)}{D} = a + \frac{b}{T} \quad (10)$$

All these relationships will, of course, give differing values of $\frac{\partial^2}{\partial T^2} \left(\frac{1}{D} \right)$ and hence of ΔC_p ; actually, equation 9 gives ΔC_p as zero, and, from this point of view, is ruled out.

It seems plain, therefore, that the correct relation between dielectric constant and temperature has yet to be discovered, and consequently it is not possible at present to link equation 4 with the $\log K - 1/D$ expression satisfactorily. It also follows that the division of ionic energies in solution into two parts, while no doubt a very useful hypothesis, has not been given any quantitative support in this field of inquiry.

It may be readily conceded that equation 4 co-ordinates the dissociation constant-temperature data within the experimental range (just as Harned's equations do). No doubt, also, it is a more useful equation in some cases, but not always; definitely it is not so for propionic acid, and scarcely so for acetic acid if the two extreme temperatures are excluded. The assumption of a temperature invariant ΔC_p (not used by Harned) applies in the limited experimental range, but the use of the resulting equation (derived by using such an assumption) for the purpose of extrapolation will need support from other directions. It can be shown here that such support is not yet forthcoming (see § 3).

The temperature invariance of ΔC_p in chemical reactions has not been proved. On the contrary, Lewis and Randall¹⁴ give many instances of reactions in which ΔC_p varies linearly or even quadratically with temperature. Also, Pitzer⁷ has measured the heat of ionisation of water, using Rossini's deduction,¹⁵ viz., $\frac{\partial \Delta C_p}{\partial T} = -0.3$.

Thus, if ΔC_p varies specifically for each substance with respect to temperature, the values of ΔH_0 , calculated by plotting

$$\left(\log K - \frac{\Delta C_p}{R} \log T \right)$$

against $1/T$, apart from having no absolute significance, may also have no relative value; that this is likely is implied by the incongruous orders of acid strengths predicted by the ΔH_0 values. It is our conclusion, therefore, that equation 6 belongs to the class of equations adequate enough in the experimental range, but not reliable for extrapolation purposes.

3. The Influence of Constitution on Acid Strengths.

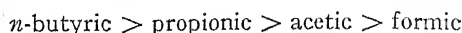
On the basis of these values of ΔH_0 , Everett and Wynne-Jones⁸ arrive at certain new conclusions regarding constitutional influence on the strengths of organic acids (ΔH_0 is taken to represent relative "intrinsic strength").

¹³ Onsager, *J. Am. Chem. Soc.*, 1936, **58**, 1486.

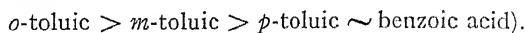
¹⁴ Lewis and Randall, *Thermodynamics*, pp. 103, 174, etc., McGraw Hill, 1927.

¹⁵ Rossini, *Bur. Standards J. Research*, 1930, **4**, 313.

Among the groups of acids to which these authors devote particular attention are the simple fatty acids, formic to *n*-butyric, and the following sequence of "intrinsic strengths" has been put forward :—



(compare also the order :—



This is clearly opposed to the mass of other evidence provided by studies of benzene orientation, reaction kinetics, etc., which indicate that alkyl, attached to carbon, invariably initiates electron release (general inductive effect).

In support of the foregoing contention it was stated that in the log K — T plot the curves for acetic and *n*-butyric acids cut at -10°C . when extrapolated. This, however, does not invalidate the statement made by one of us¹⁶ that, so far, there exist no *experimental* data showing that ionisation constants at different temperatures present different relative orders. In any case, if this extrapolation were accepted it would simply serve to show that the enhancement of strength of *n*-butyric acid, already regarded by us¹⁷ as anomalous, becomes more

marked at lower temperatures, and, actually a disturbance of the kind that we envisaged might easily lead to such a tendency.*

The explanation advanced to account for the anomaly proposes that in *n*-butyric acid there is an interaction between carboxyl and the terminal methyl group, due to a restricting potential arising from attraction between the $\text{C}-\text{CH}_3$ and $\text{C}-\text{O}$ dipoles, possibly showing

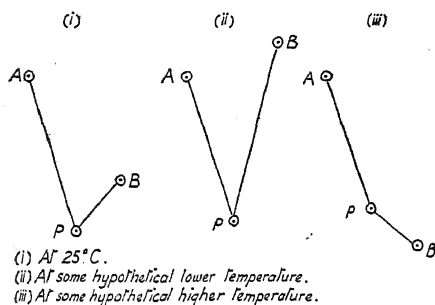


FIG. 1.

itself in hydrogen bonding which is effected by maintenance of the *cis* position (compare reference 19). In consequence of the existence of this additional influence in *n*-butyric acid (and higher homologues) it follows that as the temperature falls the maintenance of the *cis* position is favoured (caused by a diminution in rotational energy which in turn renders the dipole attraction more effective), and the part played by this influence in determining the strength of the acid becomes proportionately greater, *viz.*, the anomaly becomes more marked, whereas elevation of temperature has the converse effect. Thus it is possible that over a range of temperature the ionisation constants of the three simplest fatty acids (A, acetic; P, propionic; B, *n*-butyric) might present, on comparison, the sequences represented diagrammatically in Fig. 1 (in which A and P will always bear much the same

¹⁶ Dippy, *J. Chem. Soc.*, 1937, 1776.

¹⁷ *Ibid.*, 1938, 1222; Jenkins and Dippy, *J. Am. Chem. Soc.*, 1940, 62, 483.

* It was contended long ago that intramolecular disturbances in acids such as *p*-nitrophenol were responsible for abnormal temperature dependence (see reference 18); although it is not necessarily implied here that *n*-butyric acid is analogous to this.

¹⁸ Walden, *Das Leitvermögen der Lösungen*, vol. 1, p. 100, 1934, for details.

relation to each other). But, as already indicated, the experimental evidence goes only as far as to show that the curve for *n*-butyric acid, obtained by plotting $\log K$ against T (Fig. 2), tends to converge to that of acetic acid at lower temperatures, and to diverge from it at higher temperatures, and so approach very near to that of propionic acid. Thus sequence (i) has alone been encountered so far.

It seems important, therefore, to identify the displacement of the $\log K$ - T curve for *n*-butyric acid with the alleged anomaly of the acid. The singular character of this displacement is clearly repre-

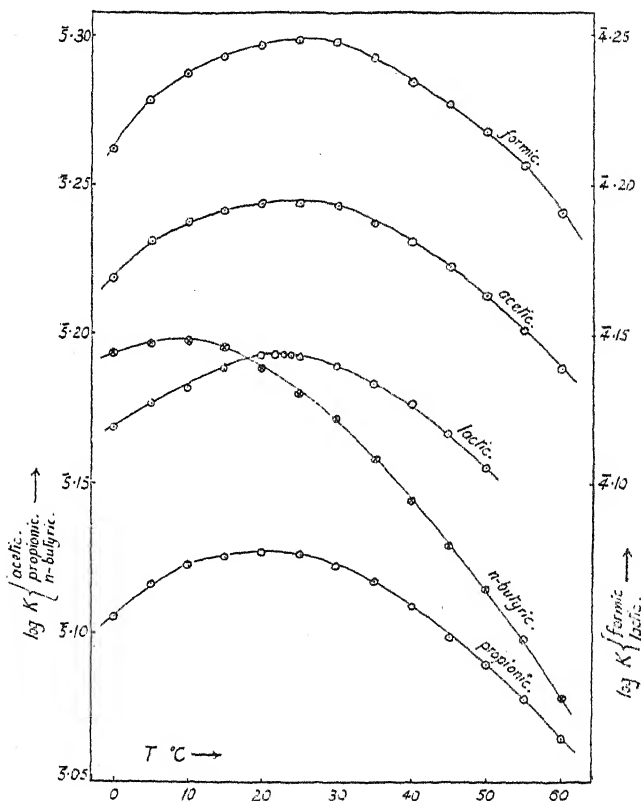


FIG 2.*

sented in Fig. 2 which includes altogether the curves for four other acids ranging in strength (K) from 10^{-5} to 10^{-4} but which give similar values of θ (21° to 25° C.) in contrast to that for *n*-butyric acid (8° C.). Indeed the curves for the other acids arrange themselves in such a way that, in order to gain "inversion" of strengths, extrapolation over a very wide temperature range becomes necessary, e.g., over at least 100° in the case of formic and propionic acid, which is not at all permissible, good as Harned's data are.

* The data used here are due to Harned and co-workers,^{1a, b, c} except those for lactic acid, due to Martin and Tartar.^{3a}

A further significant fact is that the temperature dependence of *n*-valeric acid appears to resemble that of *n*-butyric acid (the theory of the anomaly embraces all *n*-fatty acids from butyric acid upwards). It can be seen from Jahn's measurements,^{4b} conducted in 10° intervals over the range 10° to 40° C., that *K* for *n*-valeric acid steadily diminishes, *i.e.* *K*_m occurs at some temperature below 10° C. The values in question are classical constants and are only approximate, but they are

TABLE II.—*n*-VALERIC ACID.

<i>T</i> °C. 10 ⁵ <i>K</i>	10 1·85	20 1·78	30 1·67	40 1·56
--	------------	------------	------------	------------

tained in Table II exclude measurements made at concentrations greater than *N*/32.

Other doubtful conclusions arise from an analysis of ΔH_0 data. For example, examination shows that the ΔH_0 values for propionic and monochloroacetic acids are almost identical; this opposes the view that the chlorine substituent is powerfully electron-attractive, a belief so well substantiated by dipole moment data and measurements of reaction velocities for numerous systems. On the other hand, it is noteworthy that the ionisation constants for the three chloroacetic acids in water at 25° are in harmony with these facts, and, also, have been successfully correlated with the number of possible resonance structures in these systems,¹⁹ a procedure which has already been given independent support.²⁰

The conclusions which have been reached by Everett and Wynne-Jones in connection with substituted benzoic acids are no more easily reconciled; actually here the values of ΔH_0 have been derived from the far less satisfactory data of Schaller. It cannot be too strongly emphasised that classical ionisation constants obtained by the old technique, involving, for example, the crude method of successive dilution, should be regarded as undesirable data where critical quantitative deductions are concerned. It is not surprising, therefore, that the values of ΔH_0 accorded to *m*-nitro- and *m*-iodo-benzoic acids imply that these acids are *weaker* than the parent acid, an observation in conflict with the known polar influence of these substituents.

In conclusion, it must be remembered that acid ionisation constants for aqueous solutions at 25° C. have been found consistently to reveal well-defined regularities, and apart from this, they have on countless occasions shown marked agreement with observations in other fields of investigation. It seems scarcely likely that this striking co-ordination of facts is simply fortuitous. Actually, not only is qualitative agreement widely encountered (*i.e.* based on sequences of acids), but quantitative relationships, mostly having a distinct theoretical basis, have been satisfactorily tested with such data, as for instance the equation connecting *K* with dielectric constant of medium,¹¹ and again the correlation²¹ of *K* with electrostatic potential, as derived from recorded dipole moments and interatomic distances.

¹⁹ Jenkins, *Nature*, 1940, 145, 625; *J. Chem. Soc.*, 1940, 1447.

²⁰ Bell, *Nature*, 1940, 146, 166.

²¹ Jenkins, *J. Chem. Soc.*, 1939, 640, 1137.

We submit, therefore, in consequence of the arguments set out above, that despite criticisms which have been advanced, there is very good reason for believing that the ionisation constants for aqueous solutions at 25° C. provide at least as good a measure of true acid strength as any other quantity yet proposed. Until there exists a vastly greater body of suitable ionisation constant-temperature data, it is unlikely that the position will be clarified further.

Note added 2nd January, 1941.

Since the preparation of this paper a note on the temperature variation of the ionisation constants of weak electrolytes has been published by Harned and Robinson (*Trans. Faraday Soc.*, 1940, **36**, 973) which constitutes an examination of the suitability of five selected equations to represent the existing data. Three of these equations (two proposed by Harned and one by Everett and Wynne-Jones) were found to be satisfactory within the experimental error, although one of Harned's was preferred as it introduces less labour in manipulation. It is noteworthy that this contended equality of the equations is completely in line with the arguments advanced in the present article, but whereas Harned and Robinson have omitted to examine the merits of Everett and Wynne-Jones's detailed conclusions, reached on the assumption of the superiority of their own equation, we have sought to place these in their proper perspective.

Summary.

A review is made of the data so far recorded for the variation of the ionisation constants of monocarboxylic acids with temperature, and the relationships advanced to account for this temperature dependence are discussed critically. It is claimed that the tendency to regard these equations as extrapolation formulæ is unjustified, and capable of leading to erroneous conclusions. This contention is made the basis of a defence of the present practice of employing thermodynamic ionisation constant data for a fixed temperature and aqueous solution, in preference to other quantities, as a measure of true acid strength.

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THE THERMODYNAMICS OF ACID-BASE EQUILIBRIA.

BY D. H. EVERETT AND W. F. K. WYNNE-JONES.

Received 10th June, 1941.

The preceding paper by Dippy and Jenkins criticises many of the assumptions, conclusions and speculations which were contained in our paper with the above title.¹ As the assumptions were fully realised and explicitly stated by us, it seems hardly worth while repeating them. The speculations were admittedly tentative, but at present we see no reason for repudiating them.

¹ Everett and Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35**, 1380.

It seems, however, that the main purpose of the preceding paper is to traverse our chief conclusion that the dissociation constants of acids at a single temperature are quite unsuitable for theoretical discussions of molecular structure. The authors "repeat" a statement "that, so far, there exist no *experimental* data showing that ionisation constants at different temperatures present different relative orders," which they ascribe to Dippy.² We can give many well-established examples of inversions in the order of acid strengths. Far from being abnormal such inversions are apparently common, which is remarkable when one considers that within the small range of temperatures normally employed only acids of closely similar strength are likely to show inversion.

Of the acids examined by exact methods we have five main groups :

- | | |
|--|--------------------|
| (1) Formic, glycollic and lactic acids with values of $K \sim 10^{-4}$ | |
| (2) Acetic, propionic and butyric acids. | $K \sim 10^{-5}$ |
| (3) First dissociations of α -amino-acids. | $K \sim 10^{-2.5}$ |
| (4) Second dissociations of α -amino-acids. | $K \sim 10^{-10}$ |
| (5) The methylammonium ions. | $K \sim 10^{-11}$ |

In the first group the values of K for glycollic and lactic acids are rapidly converging and will clearly cross at about -5° . In the second group butyric acid rapidly approaches acetic acid in strength at low temperatures and propionic acid at high temperatures; the inversion points should be -10° and 75° .

The first dissociation constants of the α -amino acids afford 8 instances of inversion of strength *within the range of temperature examined experimentally* :—

alanine and amino-isobutyric acid	at 15° ,
amino- <i>n</i> -valeric acid and <i>iso</i> -leucine	at 22° ,
amino- <i>n</i> -butyric acid and valine	at 25° ,
norleucine and leucine	at 39° ,
norleucine and <i>iso</i> -leucine	at 45° ,
alanine and leucine	at 49° ,
alanine and <i>iso</i> -leucine	at 50° ,
leucine and <i>iso</i> -leucine	at 50° .

Amongst the second dissociation constants of these acids nor-leucine and amino-butyric acid change strength at 30° . In the last group the curves for the mono- and di-methyl ammonium ions will intersect at -11° .

As the phenomenon of inversion of acid strength with change of temperature is clearly established, it is obviously necessary to obtain exact values for the various thermodynamic functions relating to ionisation. The need for this is shown in the particular case of butyric acid for the anomalous strength of which Dippy and Jenkins have given a special explanation involving the conception of restricted rotation in the butyrate ion; if this explanation is correct, we should expect the partial heat capacity of the ion to be lowered and consequently ΔC_p for the ionisation to be more negative than for acetic and propionic acids; the reverse is true.

As several equations have been proposed for the temperature de-

² Dippy, *J. Chem. Soc.*, 1937, 1776. We are unable to find the statement in this reference.

pendence of dissociation constants, it appears to be thought that reliable values cannot be obtained for any of the thermodynamic functions other than ΔG° at a particular temperature.

Actually the three equations:

$$\begin{array}{llll} \log K = A/T + B \log T + CT + D & . & . & (1)^3 \\ \log K = A/T + B \log T + C & . & . & (2)^1 \\ \log K = A/T + BT + C & . & . & (3)^4 \end{array}$$

yield almost identical results for all the thermodynamic functions except the temperature coefficient of ΔC_p . With regard to this Harned and Robinson⁴ have shown that our assumption of a temperature-independent ΔC_p is not necessary, but they point out that on their assumption the temperature coefficient of ΔC_p is only 0.1 cal./deg.². The approximate and quite empirical equations of Harned and Embree⁵ and of Pitzer,⁶ while of great value for a general survey of the temperature dependence of dissociation constants and for estimating values when full data are not available, are not suitable for the exact evaluation of thermodynamic functions and, in particular cannot be expected to give correct values of ΔC_p . We pointed this out in our paper. Incidentally we made no claim for the superiority of equation (2) over equation (1); it would clearly be absurd to do so.

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³ Harned and Ehlers, *J. Am. Chem. Soc.*, 1933, **55**, 652.

⁴ Harned and Robinson, *Trans. Faraday Soc.*, 1940, **36**, 973.

⁵ Harned and Embree, *J. Am. Chem. Soc.*, 1934, **56**, 1050.

⁶ Pitzer, *ibid.*, 1937, **59**, 2365.

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COVALENCY, IONISATION AND RESONANCE IN CARBON BONDS.

BY E. C. BAUGHAN, M. G. EVANS AND M. POLANYI.

Received originally on 6th February, and as revised on 5th May, 1941.

The Three Types of Carbon Links and their Contributions to the Properties of the Ground State.

Every chemical bond is characterised by three main components, each of which is defined by an energy which is a function of the interatomic separation. These three main components (which may themselves be complex), the covalent state $A-B$ and the two ionic states A^+B^- and A^-B^+ , contribute to the energy and properties of the true ground state of the molecule, and the extent to which any particular representation participates in the ground state depends upon two factors: the energy separation of the states, and the interaction integral between them.²

We will here apply these quantum mechanical ideas to bonds involving carbon centres, and attempt to demonstrate that many of the characteristic properties of these bonds, and the influence of substituents on these properties, can be interpreted on this basis.

The CH_3-H , CH_3-Hal and $CH_3-Alkali Metal$ Bonds.

We will first apply these principles to the three bonds CH_3-H , CH_3-Hal and $CH_3-alkali metal$ as examples which are the least complex because of the simplicity of the CH_3 radical. The simplest possible case would be if the two ionic states lay so much higher in energy than the homopolar state that resonance interaction between the ionic and homopolar states would be negligibly small, and the homopolar state would be in consequence a close approximation to the ground state of the molecule for all interatomic separations. An approximation to this extreme case we consider to be found in the CH_3-H bond where, because of the high ionisation potentials of H (312 Cal.) and CH_3 (180 Cal.) and the low electron affinities of CH_3 (20 Cal.) and H (17 Cal.), the ionic curves lie very much higher than that of the ground state. The energy of the ground state as a function of the internuclear separation is known approximately from the Morse function

$$u = D(2e^{-a(r-r_0)} - e^{-2a(r-r_0)}) \quad (1)$$

requiring a knowledge of the heats of dissociation D , the normal internuclear separation r_0 , and the fundamental frequency ν . The internuclear separation and fundamental frequency are well established, but there has been some uncertainty about the correct values of D ; through-

¹ Baughan and Polanyi, *Nature*, 1940, 146, 685.

² Pauling, *J.A.C.S.*, 1932, 54, 988.

out this work we shall adopt for bond strengths the values adduced by Baughan and Polanyi¹ (see Table VII). The energies of the corresponding ionic curves $\text{CH}_3\text{-X}^+$ and CH_3X^- have been constructed from the approximate expression of Born:

$$u = -\epsilon^2/r + br^{-n} \quad (2)$$

using the knowledge of the equilibrium interionic distance and an appropriate value of the exponent n ; for the case of X^+ being the proton this approximation is inadequate, since so small an ion can penetrate into the electronic shell of the negative ion, and in this case we have adopted Pauling's² calculation for the H^+F^- ionic curve with appropriate zero. Fortunately most of the quantitative conclusions drawn are not very

TABLE I.—“PHYSICAL” VALUES FOR I_{CH_3} .

Author.	Ref.	Method.	I_{CH_3} kcal.
Frazer and Jewitt	3	Molecular beam	248 ± 15
L. G. Smith	4	Appearance potential	≤ 218
Mulliken	5	Calculated	200

sensitive to the exact value of n , as we shall show in more detail for the case of methyl iodide, and for most of the curves we have taken $n = 8$.

The relative position of the ionic curve and the Morse function at infinite separation can be defined if we know the appropriate ionisation potentials I and electron affinities E . There is much uncertainty in the values of I_{CH_3} and E_{CH_3} obtained by “physical” methods such as electron bombardment and mass spectrograph appearance potentials.

Table I gives the values of I_{CH_3} obtained by various methods and, from theoretical considerations, by Mulliken.⁵ In Appendix I we cite various chemical arguments involving the use of Born-Haber cycles, together with reasonable estimates of solvation energies, and these arguments lead to the values which we shall adopt: $I_{\text{CH}_3} = 180$ and $E_{\text{CH}_3} = 20$.

Fig. 1 shows the three energy curves computed for $\text{CH}_3\text{-H}$ in the way described here, using the fundamental data given in Table II. The striking feature of these curves is the way in which the $\text{CH}_3\text{-H}^+$ curve, although having a higher asymptotic energy value than the CH_3H^- , comes to within 160 Cal. of the ground state at the internuclear separation 1.09 Å. (the normal value for the CH bond in methane). This is because the proton is very small, and so can penetrate the electronic shell of the CH_3^- ion whereas the H^- ion has a much larger radius.

TABLE II.*—DATA FOR MORSE CURVES.

	r_0	D (kcal.)	ν cm ⁻¹	a (Å ⁻¹)
$\text{CH}_3\text{-H}$	1.09	106.5	2910	1.92
$\text{CH}_3\text{-I}$	2.10	55.8	522	1.66

* The ν 's come from Kohlrausch, *Der Smekal-Raman Effekt*, p. 154, the r_0 's from Pauling,⁷ the D 's, which include the zero point energy, from Baughan and Polanyi,¹ the a 's from these data, and the assumption of Morse's equation.

³ Frazer and Jewitt, *Proc. Roy. Soc., A*, 1937, **160**, 563.

⁴ Lincoln G. Smith, *Physic. Rev.*, 1937, **51**, 263.

⁵ Mulliken, *J. Chem. Physic.*, 1933, **1**, 492.

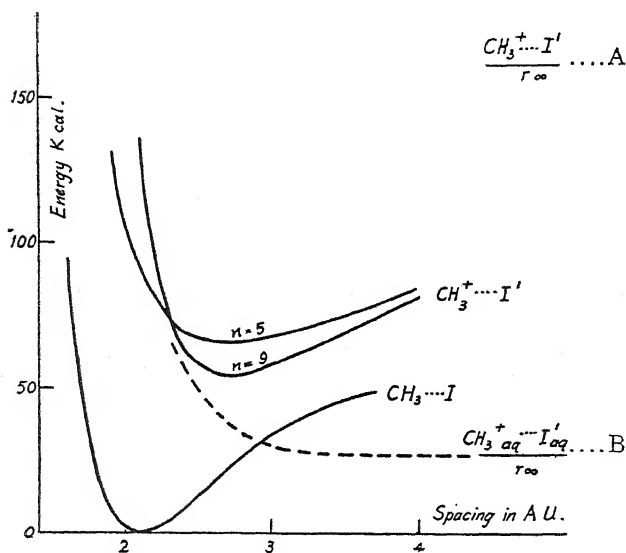
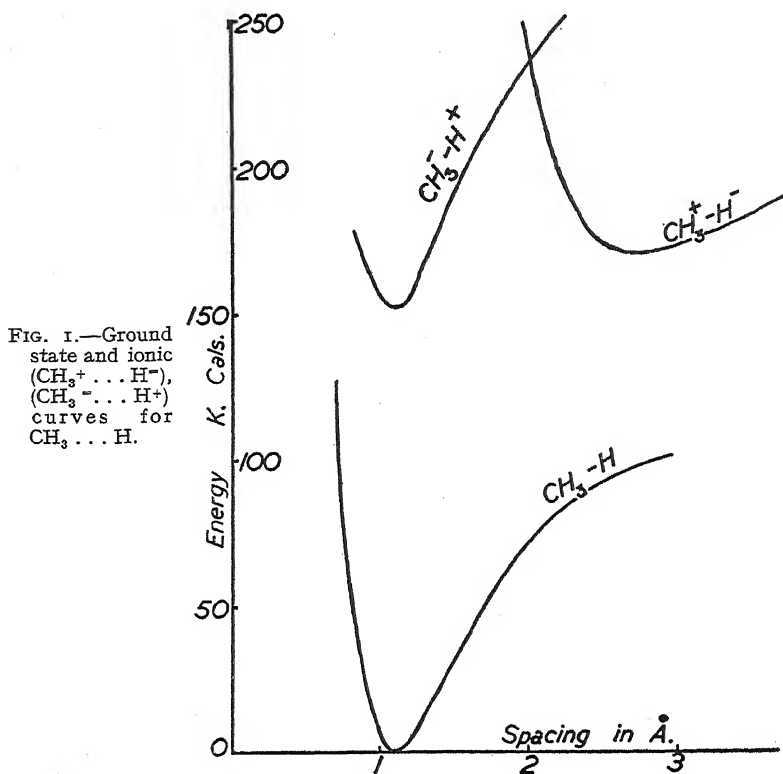


FIG. 2.—Ground state and ionic ($\text{CH}_3^+ \dots \text{I}'$) curves for CH_3I ; ionic values at infinite distance in vacuo (A) and in water (B).

Using the Morse curve for the ground state and Born's approximation for the ionic curve, we have in Fig. 2 constructed curves for the CH_3I molecule. Here we show only the CH_3^+I^- curve, since the CH_3-I^+ lies so much higher in energy. In this case we give also a curve in Fig. 3

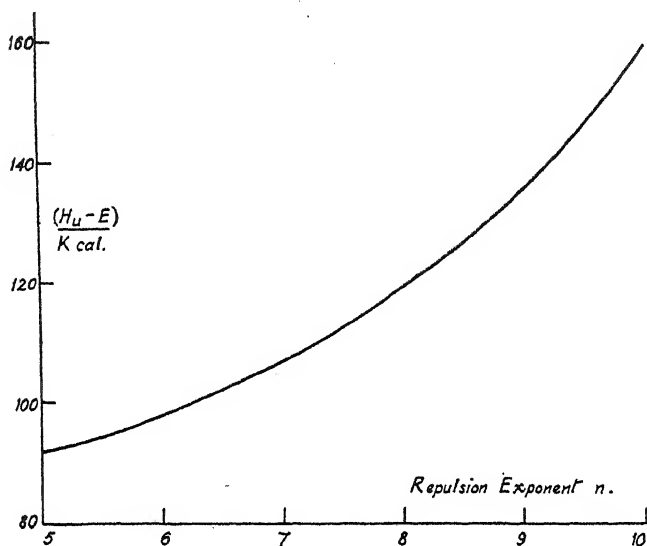


FIG. 3.—
Dependence of
($H_u - E$) on
 $n(\text{CH}_3 \dots \text{I})$.

showing the dependence of the energy separation between the ground and ionic states at the observed internuclear distance on the value of the exponent in equation 2. Between the values $n = 7$ and $n = 9$, both of which are reasonable, the separation is not highly sensitive to the value of n , and hence the quantitative conclusions which we will draw later are not due to our particular choice of $n = 8$. The data for the construction of these two curves using equations 1 and 2 are given in Table II. There is one point deserving special discussion: in constructing the CH_3^+I^- curve we have taken a value of r for $\text{C}^+ = 0.56$ Å. Our reasons for this choice are (1) the co-ordinate in which we are interested is that representing the approach of an iodine ion to the carbon centre of the CH_3^+ ion, and for this to be comparable with the CH_3-I homopolar curve the CH_3^+ ion must be treated in the same configuration as that in the CH_3-I molecule. (2)

It appears from the atomic and ionic radii listed by Sidgwick,⁶ that the contraction of an atom resulting from the removal of electrons is, in the same periodic group, directly proportional to the number of electrons removed and the contraction

TABLE III.

	Neutral.	+2	+4	Contraction per Electron.
Si ¹⁷	1.17	—	0.40	0.19
Ge	1.22	—	0.44	0.19
Sn	1.51	—	0.74	0.19
Pb	1.75	1.32	0.84	0.22, 0.23

per electron removed is about the same for all elements. Thus for the carbon group. A mean value of 0.21 Å. for the contraction per

⁶ Sidgwick, *The Covalent Link in Chemistry* (Cornell University Press), p. 83, 1933.

electron in group IV leads to a value of $(0.77 - 0.21) = 0.56$ A. for a singly charged carbon atom.

All other ionic radii and observed internuclear separations are taken from data given by Pauling.⁷

A third and very interesting case is that shown in Fig. 4 for the CH_3Na molecule.

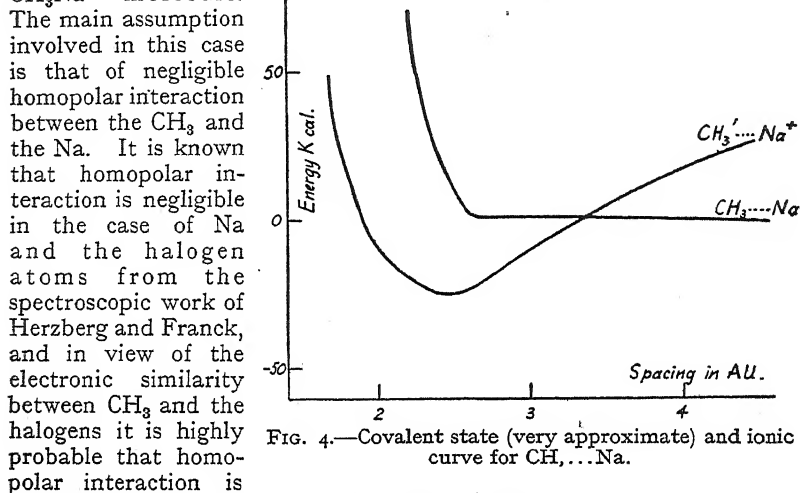


FIG. 4.—Covalent state (very approximate) and ionic curve for $\text{CH}_3\text{...Na}$.

The striking difference between the curves shown in Fig. 4 and those of Figs. 1 and 2, is that the ionic curve lies lower in energy than the homopolar state of the molecule at separations near the equilibrium value.

Having described the construction of these curves, we will now discuss the chemical and physical properties of the bonds in terms of them.

The Relation between Dipole Moments, Resonance Energy, and the Energy Separation between the Ground and Ionic States.

The ground state of a molecule can be represented by a ψ function which can be written in terms of ψ_h and ψ_i for the homopolar and ionic states.

$$\psi = a_1\psi_i + a_h\psi_h \quad \text{where} \quad a_1^2 + a_h^2 = 1.$$

The energies of the ground state E and the homopolar H_{hh} and ionic H_{ii} states are related by the equations

$$\begin{aligned} a_1(H_{ii} - E) + a_h(H_{ih} - \delta_{ih}E) &= 0 \\ a_1(H_{ih} - E) + a_h(H_{ih} - E) &= 0 \end{aligned}$$

where

$$H_{ii} = \int \psi_i H \psi_i d\tau \text{ etc.}$$

Thus, as Wall⁸ has shown

$$\alpha^2 = \left(\frac{a_1}{a_h}\right)^2 = \frac{H_{hh} - E}{H_{ii} - E} \quad \dots \quad (3)$$

⁷ Pauling, *The Nature of the Chemical Bond* (Cornell University Press), 1939.

⁸ F. T. Wall, *J.A.C.S.*, 1939, **61**, 1051; 1940, **62**, 800.

The term $(H_{\text{hh}} - E)$ is the resonance energy in the ground state arising from the interaction between the ionic and homopolar states $(H_{\text{II}} - E)$ is the difference in energy between the ground and ionic states; its value in any particular case can be obtained by the methods described above.

The coefficients a_1^2 and a_h^2 measure the probability of the ionic and the homopolar states participating in the ground state, and hence a_1 is related to the dipole moment μ of the bond by

$$\mu = a_1^2 e r_0 \quad (4)$$

where r_0 is the normal separation and e the electronic charge. This is the usually adopted form of the connection between μ and a_1^2 if it be assumed that ψ_i and ψ_h are mutually orthogonal.

Thus, by combining equations (3) and (4), we have a means whereby, knowing the dipole moment μ and the energy separation $(H_{\text{II}} - E)$ we can calculate the resonance energy R_{th} , or alternatively, if we know $(H_{\text{II}} - E)$ and R_{th} (or changes in R_{th} from a fixed value in a homologous series), we can calculate μ or the corresponding changes in μ .

Pauling⁷ has shown that for a number of diatomic molecules AB with similar centres the homopolar bond strength AB is given by

$$AB = \sqrt{(AA) \times (BB)} \quad (5)$$

and has identified the difference between the observed bond strength of AB, and that given by the geometric mean, with the resonance energy arising from the participation of other states.

Although this gives very good values in a number of cases, there are marked failures of this rule. These occur, as Mulliken⁹ has shown, where the electron configurations of the atoms or centres in AB are of very different types. Thus, for molecules such as NaCl, CH_3I , we should expect wide deviations from this rule of the geometric mean. In many

TABLE IV.—CALCULATED IONIC RESONANCE ENERGIES COMPARED WITH THOSE FROM THE GEOMETRIC MEAN RULE.

	Calculated.	Geometric Mean.
$\text{H}_3\text{C}-\text{F}$	$\left\{ \begin{array}{l} 47 \ (n=6) \\ 62 \ (n=8) \end{array} \right\}$	43
$\text{H}_3\text{C}-\text{Cl}$	45 $(n=8)$	32
$\text{H}_3\text{C}-\text{Br}$	32 $(n=8)$	6
$\text{H}_3\text{C}-\text{I}$	23 $(n=8)$	0
$\text{H}_3\text{C}-\text{H}$	~ 9	8

cases, however, Pauling's rule will afford yet another quantitative check on the applicability of the ideas outlined above.

As an example of the way in which we shall treat the interconnection of these quantities $(H_{\text{II}} - E)$, R_{th} and μ , we will choose the CH_3-H bond. From the potential energy curves constructed above, we have the value of $(H_{\text{II}} - E) = 155$ Cal. at the normal internuclear separation of 1.09 Å. The value of

the CH dipole moment is given as 0.3 by Hirschfelder (quoted by Pauling)⁷; this leads to a value of $(a_1/a_h)^2 = 0.06$, which on the basis of equation (4) gives a value for R of 9.3 Cal. Using the values D for $\text{CH}_3-\text{CH}_3 = 88$ Cal. and $D_{\text{H}-\text{H}} = 103.4$ Cal.,¹ the geometric mean gives a value for the homopolar CH_3-H bond of 95.5 Cal., and thus to a resonance energy R_{th} of 8.1 Cal., comparing well with the value obtained from the dipole moment and the energy separation. Alternatively, we could have taken the value of R_{th} from the difference between the observed value of $D_{\text{CH}_3-\text{H}}$ and that given by Pauling's rule, and then

⁹ Mulliken, *J. Chem. Physics*, 1934, 2, 782.

using the value of $(H_{11} - E)$, computed the bond dipole moment. In the later part of this work we shall calculate changes in dipole moment in this way since the analysis of bond strengths made by Baughan and Polanyi¹ enables us to obtain the changes in $(H_{11} - E)$ and in R_{1h} . Similar calculations of the value of R_{1h} from the dipole moment of the bond and from the calculated value of $(H_{11} - E)$ can be made from the CH_3 halides. These results are shown in Table IV.

In the series methyl fluoride, chloride, bromide, iodide, we should expect a parallel change in $(a_1/a_h)^2 = \mu/er_0$ and the resonance energy, since in this sequence the value of $(H_{11} - E)$ becomes progressively larger because of the decreasing electron affinity of the halogen atom and the increasing radius of its ion.

In this sequence, however, comparison with the rule of the geometric mean gives bad agreement for bromine and iodine (see Table IV). This is not surprising, since we would expect the applicability of this rule to fail as the centres CH_3 and halogen become more dissimilar and, indeed, the rule leads to the improbable result that there is an absence of resonance between the ionic and homopolar states in CH_3I which would imply the absence of a bond dipole moment and identical electronegativities of CH_3 and I. This result is extremely improbable (e.g. iodoacetic acid is almost as strong an acid as chloroacetic), and this difficulty does not arise because of the values of the bond strengths chosen, since it is also present where "average" bond strengths are used (see Pauling,⁷ p. 69), and must therefore be due to a breakdown of the geometric mean rule.

Electrolytic dissociation of the C—H and C—Hal bonds.

Figs. 1 and 2 represent the energy relations between the ground and ionic states for the isolated molecules. If we wish to discuss the behaviour of these molecules in solution, we must take into account the interactions between the various species and the solvent molecules. Thus, in the case of the $\text{CH}_3\text{—H}$ link although, because of the high ionisation potential of the H atom, the asymptote of the $\text{CH}_3\text{—H}^+$ curve lies in vacuo higher in energy than that of the CH_3^+H^- , in aqueous solution the reverse is the case, since the heat of solvation of the CH_3^- and H^+ ions is much greater than that of CH_3^+ and H^- . Except for the special case of the proton these heats of solvation have been computed by the method used by Bernal and Fowler,¹⁰ and Eley and Evans,¹¹ and the following ionic radii have been taken: $\text{H}^- = 2.10$ (the value given by Pauling⁷) $\text{CH}_3^+ = 1.4$. It will be noted that this value is not the same as that used for the construction of the ionic state CH_3^+I^- in Fig. 2. There is the important difference in the two cases that the halogen ion approaches, as we have mentioned, the C centre of the CH_3^+ ion, while in solution where the CH_3^+ ion is completely surrounded by water molecules the field set up will be roughly spherically symmetrical and the radius approximate to the effective radius of an NH_4^+ ion, which is 1.48 Å. For the CH_3^- ion we have expanded a methane molecule by the value for the expansion of the carbon centre to that of C^- and so, assuming this ion also to be spherically symmetrical in solution, get a value 2.1 Å. Values of the heats of solvation based on these radii are given in Table V, together with the value 282 Cal. obtained for the

¹⁰ Bernal and Fowler, *J. Chem. Physics*, 1933, 1, 515.

¹¹ Eley and M. G. Evans, *Trans. Faraday Soc.*, 1938, 34, 1093.

proton.¹² (It is perhaps worth inserting here that the value 47 Cal. for the solvation heat of H^- yields by an obvious cycle the value + 56 Cal. for the reaction $H'_{aq} + H_2O \rightarrow OH'_{aq} + H_2 \text{ gas}$).

By this means, if we neglect the small heats of solvation of the molecules in their ground states, we can find the heat of such reactions as $CH_4 \rightarrow CH_3'_{aq} + H'_{aq}$ and $CH_3I \rightarrow CH_3'_{aq} + I'_{aq}$ from the known

TABLE V.—IONIC HEATS OF SOLUTION IN WATER.

Ion.	Radius (A.).	Heat Solution (kcal.).
CH_3^+ . .	1.48	95
CH_3^- . .	2.1	47
H^+ . .	—	282
H^- . .	2.10	47

potential energy curves and the solvation heats, which evidently give the limiting value when the ions have no influence on one another's solvation heats (therefore at infinite distance). The complete plotting of such a curve as that of the interaction between CH_3^+ and I^- in water can be carried out, either by an extension of the methods of Bernal and Fowler, or alternatively by considering the $CH_3^+I^-$ near its equilibrium distance as a dipole of $\mu = er$, and applying the formula of Kirkwood¹³ for the heat of solution of a dipole. Both methods agree in predicting the course of the $CH_3^+I^-$ curve in water to be practically horizontal from infinite distance right in to the crossing of the ionic and Morse curves at about 2.6 A. The height of this cutting point rounded off slightly for resonance gives then the activation energy of the process CH_3I to $CH_3^+ + I^-$ as ~ 30 Cal., which, if the curve is horizontal, should be identical with the heat of ionisation. Our choice of 180 Cal. for the ionisation potential of CH_3 , which was consistent with the equilibrium dissociation of methyl halides, thus provides a reasonable value for the activation energy of this dissociation agreeing with that found by Ingold.¹⁴

Similar arguments would predict that if sodium methyl could be dissolved in water without reaction, it would be a strong electrolyte, since the covalent curve is practically flat and the sum of solvation heats (160 Cal.) is greater than the difference (98 Cal.) between the ionisation potential of sodium and the electron affinity of CH_3 . Hence at large distances the ionic curve in the solvent lies well below the covalent curve. In agreement with this, the alkali metal alkyls show a conductivity¹⁵ in solution in zinc diethyl which is about what would be expected, from the Bjerrum-Fuoss¹⁶ theory of ion association, for a true salt in such a solvent. Again, we would predict that methane should show no acid properties in water, or even exchange hydrogens, since our values lead to the prediction $CH_{4aq} \rightarrow CH_3'_{aq} + H'_{aq} - 70$ Cal.

The idea of resonance between homopolar and ionic states provides therefore an explanation of the energies of formation of methyl derivatives in terms of their dipole moments or vice versa, and the ideas used explain the electrolytic behaviour of such compounds. In the next section we consider the effects of a second type of resonance: resonance of the alkyl radicals among various canonical forms.

¹² Baughan, *J. Chem. Soc.*, 1940, 1335.

¹³ Kirkwood, *J. Chem. Physics*, 1934, 2, 351.

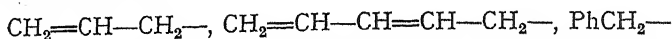
¹⁴ Ingold and co-workers: numerous papers in *J. Chem. Soc.*, particularly 1937.

¹⁵ Hein. Results quoted by Wooster, ref. 24.

¹⁶ Fuoss, *Trans. Faraday Soc.*, 1934, 30, 967.

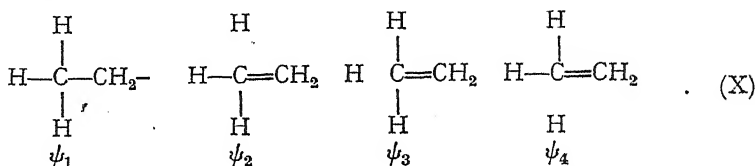
Resonance Energy of Alkyl Radicals and its effect on the Properties of Bonds.

One type of resonance of the free radical is well recognised ; it occurs in such structures as



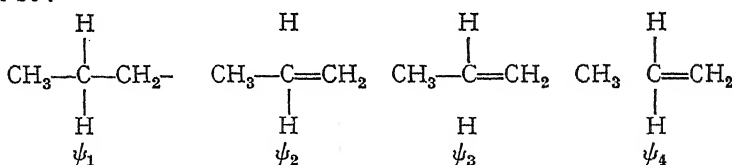
wherever an unsaturated or conjugated group is attached to the carbon centre of the free radical.

The second type of resonance is possible in the radicals of saturated hydrocarbons, and was first mentioned by Wheland.¹⁷ The bond representation of the various resonating states in, for example, the ethyl radical are :—



and these types can readily be extended to the $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \\ \diagdown \\ \text{CH}_3 \end{array}$ and

$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}_3-\text{C} \\ \diagdown \\ \text{CH}_3 \end{array}$ radicals. Thus, for sec. propyl there are seven, and for tertiary butyl ten canonical states. We will expand this idea to include radicals of the type $\text{CH}_3-\text{CH}_2-\text{CH}_2\cdot$ in which the bond representations will be :



The resonance energy arising from the interaction between these four forms will not be the same as that given in the case of $\text{CH}_3-\text{CH}_2\cdot$ because of the difference in the centres and in their exchange integrals. Again, the type of canonical structure shown above can be extended to the radicals

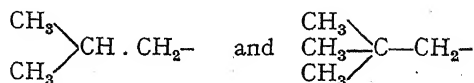


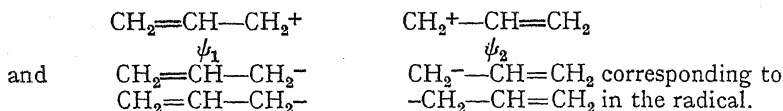
TABLE VI.—CALCULATED RADICAL RESONANCE ENERGIES.

Radical.	$\text{CH}_3\cdot$	$\text{C}_2\text{H}_5\cdot$	$n\text{-C}_3\text{H}_7\cdot$	$\text{sec-C}_3\text{H}_7\cdot$	$\text{tert-C}_4\text{H}_9\cdot$	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \cdot \text{CH}_2\cdot \\ \diagdown \\ \text{CH}_3 \end{array}$	$(\text{CH}_3)_3\text{CCH}_2\cdot$
Resonance Energy .	Calcd. 0 Obs. 0	7.05 7.2	8.62 8.1	14.10 12.6	21.15 16.7	10.19 —	11.8 —

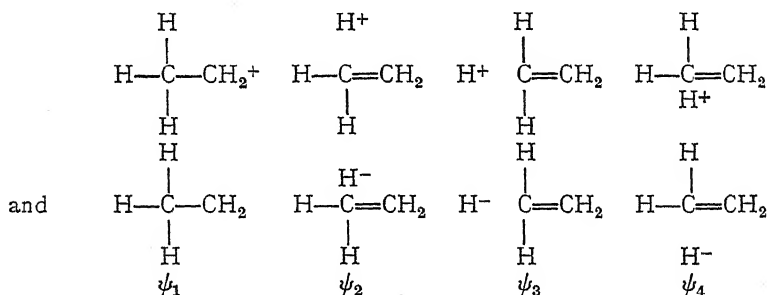
¹⁷ Wheland, *J. Chem. Physics*, 1937, 2, 479.

It is possible by the method of "bond eigenfunctions" developed by Eyring¹⁸ and his co-workers to compute the resonance energy of these radicals, and Table VI. gives the results obtained by a fairly approximate computation.

It is important to realise that such resonance is also possible in the positive and negative ions corresponding to these radicals. Thus, in the ions $(\text{CH}_2=\text{CH}-\text{CH}_2)^+$ and $(\text{CH}_2=\text{CH}-\text{CH}_2)^-$ we have



In this case the structures involve only the mobile electrons in the potential field of the three carbon centres, and in each case the energies of the forms ψ_1 and ψ_2 are the same. A calculation of the resonance energy in the above cases shows that it is approximately the same for the radical and the two ions. This may not be so for the radicals of saturated hydrocarbons. The ionic forms corresponding to X for the ethyl radical are :—



The greatly increased size of the H^- ion over the H atom brings into play strong repulsive energies which lift the energies of states ψ_2, ψ_3, ψ_4 in the negative ion far above that of the state ψ_1 . For the positive ion, although the ionisation potential of the H atom is large, the small radius of the proton involves much smaller repulsive energies and brings the energies of ψ_2, ψ_3, ψ_4 much nearer to that of ψ_1 . Thus, in this case we might expect comparable resonance energy in the radicals and the positive ions, but much smaller resonance energies in the negative ion.

If there were no interaction between the ionic and homopolar states of a molecule (the state of affairs approximately realised when the energy of separation $(H_{11} - E)$ is very large), or if there were no change in the resonance energy of the ion R^+ , then changes in the bond strength $\text{C}-\text{X}$ in a series of molecules $\text{R}-\text{X}$ would be entirely accounted for by the changes in the resonance energy R_r of the radical R, since the asymptotic energy value, but not that at the equilibrium separation of RX , is effected by the resonance energy (see Fig. 5). We have shown, however, that in most cases there is an appreciable resonance energy R_{11} between the ionic and homopolar states of the molecule and that the

¹⁸ Eyring and Kimball, *J. Chem. Physics*, 1933, 1, 239, and later papers in this journal.

magnitude of this energy is effected by the energy height of the ionic state. In changing the radical R in the molecule R—X, not only do we alter the asymptotic value of the homopolar energy curve through the radical resonance energy, but at the same time we alter the energy of the ionic state over the whole range of separation by the resonance energy of the R⁺ ion. This involves a decrease in the energy separation ($H_{ii} - H_{hh}$) at the equilibrium distance by an amount equal to the resonance energy of R⁺, and consequently an increasing resonance R_{ih} between ionic and homopolar states. Thus the bond strength is affected by two opposing influences (1) the increase in resonance energy of the radical tending to weaken the bond, and (2) the increasing interaction between ionic and homopolar states which tends to increase the bond strength

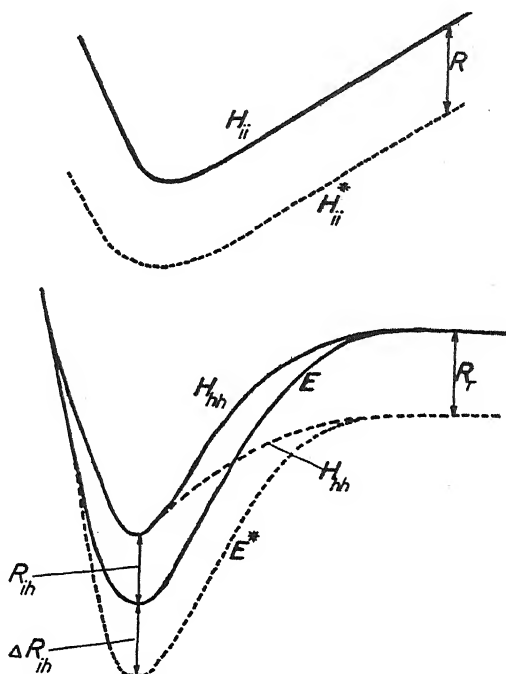


FIG. 5.— H_{ii} , H_{hh} , E (full lines): three curves for non-resonating radical. H_{ii}^* , H_{hh}^* , E^* (dotted lines): three curves for resonating radical.

$$\Delta D = -\Delta R_r + \Delta R_{ih} \quad (6)$$

These changes are shown diagrammatically in Fig. 5. Changes in the value of R_{ih} attendant upon changes in the energy separation ($H_{ii} - H_{hh}$) will also cause changes in the dipole moment of the bond, and we will now apply these ideas to the bond strengths given by Baughan and Polanyi¹ and to the dipole moments of these bonds.

TABLE VII.—BOND STRENGTHS OF R—X BONDS.

R.	R—H.	R_r .	R—I.	ΔR_{ih}	R—CH ₃ .	ΔR_{ih} .	R—OH.
Methyl .	103.6	0	55.0	($\equiv 0$)	88.2	$\equiv 0$	87.6
Ethyl .	96.4	7.2	51.2	3.4	83.4	2.4	86.2
n-Propyl .	95.5	8.1	50.7	3.8	82.8	2.7	86.7
sec-Propyl .	91.0	12.6	48.4	5.9	80.2	4.5	86.5
tert-Butyl .	86.9	16.7	46.3	8.0	76.9	5.4	87.6

Application to Changes in Bond Strengths and Dipole Moments.

We showed in an earlier section that the magnitude of the resonance energy R_{1h} in the C—H bond is small and insensitive to changes in $(H_{11} - E)$. This is evidenced by the small values of the C—H dipole over a wide series of hydrocarbons. Thus it is safe to assume that the changes in the CH bond strengths shown in Table V. are due practically entirely to the changes in resonance energy of the radical. It is interesting that the values of R_r shown in Table V, on the assumption that R_r is zero for CH_3 , (which are given as "observed" in Table VI.), agree remarkably well with those calculated in the former section.

Thus having deduced values for R_r in this series, changes in the bond strengths of R—I, for example, can be accounted for in terms of the magnitudes of R_r and R_{1h} . Since these bond strengths decrease less than for R—H on going from methyl to tertiary butyl, it is clear that the value of R_{1h} must increase in this sequence, through the closer approach

TABLE VIII.*—COMPARISON CALCULATED AND OBSERVED DIPOLE MOMENTS FOR ALKYL IODIDES.

Alkyl Radical.	μ_{obs}^{19}	$\mu_{\text{calc.}}$
Methyl .	1.64	1.64 assumed
Ethyl .	1.87	1.86
<i>n</i> -Propyl .	2.01	1.89
<i>sec</i> -Propyl .	2.12	2.04
<i>tert</i> -Butyl .	2.14	2.26

* Assuming $H_{11} - E$ for methyl iodide = 120 Cal. ($n = 8$), whence from $\mu = 1.64$, $R_{1h} = 23.0$ Cal.; other R_{1h} 's from this and the ΔR_{1h} values in Table VII.

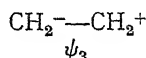
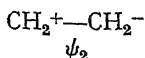
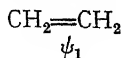
¹⁹ Groves and Sugden, *J. Chem. Soc.*, 1937, 158; the values for *sec*-propyl and tertiary butyl come from a private communication of Professor C. P. Smyth to the authors.

of the ionic curve. This corresponds to the known increase in bond dipole moments in this series, and changes in μ can be calculated in the following way. In section 2 we computed from the observed moment for methyl iodide, and the value of $(H_{11} - E)$ obtained from the potential energy curves in Fig. 2, the value of R_{1h} in methyl iodide. Using the radical resonance energies obtained from the C—H bond strength, the strengths of the R—I bonds, and this value of R_{1h} for the methyl iodide molecule, we can then assign values to R_{1h} for all the iodides listed in Table V. Further, using the previous assumption made that the resonance energy of the positive

ion is the same as that of the radical, we can obtain values for $(H_{11} - E)$ throughout the series; this assumption is not very important since $(H_{11} - E) \gg R_r$. Thus, from the potential energy curves and dipole moment for methyl iodide, and the ΔR_{1h} values for the other alkyl iodides we can calculate their corresponding dipole moments.

Table VIII gives the magnitudes used in this calculation and the results obtained. These are seen to compare well with the experimental values.

The changes in the energy required for the opening of the double bond require some consideration. Thus, the ground state of ethylene results from resonance between the following



in which the forms ψ_2 , ψ_3 have identical energies. Fig. 6 shows the relative positions of the ground and ionic states. The ground state has

been calculated as before, and the energy of the ionic state we have taken to be the sum of that of the C—C and C⁺C⁻ curves.

In the case of symmetrically substituted ethylenes, although the energy of the ground state must be lowered by the resonance of R⁺R⁻, both forms, *i.e.* R⁺—R⁻ and R⁻—R⁺, must be lowered to the same extent, and the resultant dipole will be zero, although resonance with the ionic states may be quite large. For unsymmetrical substituted ethylenes, however, the two ionic curves will be lowered by radical resonance energy by different amounts because, as we have seen, the resonance energy of a positive ion is greater than that of the corresponding negative ion. Hence, in the sequence CH₂=CH₂, CH₃—CH=CH₂, CH₃—CH₂CH=CH₂ we should expect an increasing dipole moment in the sense ⊕—⊖. There is evidence that this is true: (CH₂=CH₂ μ = 0, CH₃—CH=CH₂ μ = 0.34, CH₃CH₂CH=CH₂ μ = 0.37 from Sidgwick's²⁰ list).

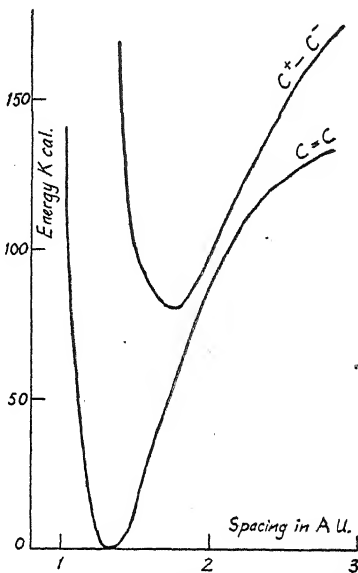
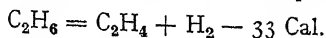


FIG. 6.—H₂C=CH₂ and CH₃⁺—CH₂⁻ curves for ethylene.

Detailed Applications.

We shall here present a few results of the application of these ideas to other problems. Of these, the first is a calculation of the proton affinity of ethylene. If the resonance energy R⁺ of a carbonium ion is approximately equal to that of the corresponding free radical, then the ionisation potential in a series of radicals is independent of their resonance energies. As in any case the resonance energy of an ethyl radical is only about 7 Cal., then the ionisation potential (I.P.) of methyl is practically equal to that of ethyl. The heat of the process



is well known. This can be dissected into the steps: C₂H₆ → C₂H₅ + H (-96 Cal. from Table V), (2) C₂H₅ → C₂H₅⁺ + electron (-I.P.), (3) C₂H₅⁺ → C₂H₄ + H⁺ (-*p*, the required proton affinity), (4) H⁺ + electron → H(+I.P. hydrogen = 312), (5) H + H → H₂ + 103.

Thus the proton affinity of ethylene is about 174 Cal. This is only about 10 Cal. less than that of water (182),²¹ but a proton affinity almost as high is required by the fact that unsaturated hydrocarbons dissolve very readily in anhydrous HF;²² the conductivity of these solutions is unfortunately not known.

It is significant that the considerable change in bond strength between methyl and ethyl halides is not clearly reflected in the rates of solvolysis.

²⁰ Sidgwick, *Trans. Faraday Soc.*, 1934, 30 (Appendix).

²¹ J. Sherman, *Chem. Rev.*, 1932, 11, 107.

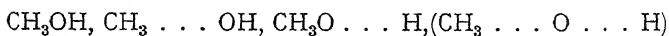
²² Klatt, *Z. anorg. allgem. Chem.*, 1937, 234, 189.

In fact, while in some solvents methyl halides show the expected slower rate of solvolysis, in others ethyl halides are hydrolysed more rapidly. We explain this by the assumption that the small size of the methyl ion increases its solvation energy to such an extent that this may offset the effects of resonance on the bond strength.

This analysis seems to throw light on the remarkably small reactivity of neo-pentyl compounds with respect to neutral solvolysis. This was proved by the observation³² that alcoholysis is very slow even at 150° C. Unpublished results by Miss Mandel in this laboratory indicate a series of velocity constants for the neutral hydrolysis of ethyl iodide, normal propyl iodide, iso-butyl iodide showing an increasing trend as they approach neo-pentyl iodide. To explain this we have to consider the fact that the resonance caused by methyl in a carbonium ion may be cancelled by substituting the H atoms in this group by methyl (*i.e.* replacing methyl by tertiary butyl); as was shown by Baker and Nathan²³ in the toluene-tertiary butyl benzene series. With this in view, it may be assumed that with regard to resonance energy the neopentyl⁺ ion is at par with the methyl⁺ ion, and its tendency to be formed by electrolytic dissociation (or "ionisation") would be equal to that of a methyl⁺ ion to which a large ionic radius is attached. With the increasing size of the ion the solvation heat falls, and therefore the activation energy of ionisation increases (see Fig. 2).

Another example is given by the reaction of sodium with hydrocarbons (see the review by Wooster).²⁴ If a C—H bond is weakened by the radical resonance energy R_r , then the electron affinity of this radical will be strengthened by $R^- - R_r$, where R^- is the resonance energy of the anion. Thus, the process $R-H + Na \rightarrow R^- + Na^+ + H$ will be aided by R^- , and that of $R + Na \rightarrow R^- + Na^+$ aided by $R^- - R_r$. The observed facts show that for the aliphatic hydrocarbon radicals R^- never becomes very large, since sodium does not react with them. For conjugated radicals, however, $R^- > R_r$. This is shown by the important work of Bent and his co-workers,³¹ and the close parallelism between the free energy changes in the reactions $R + Na$, and those in the dissociations of $R-R$ provides strong support for the principle already proposed, that the resonance possibilities of a carbanion and its corresponding free radical are very closely connected (although, for these conjugated systems, the anion resonance energies are slightly larger).

There is one point in the bond strength table (Table VII) which the present theory is unable to explain: the R—OH bond is practically constant throughout the series. This would imply, assuming equation (6), that the ionic resonance energy changes ΔR_{th} almost exactly compensated the changes in R_r the radical resonance energy. The dipole moments, however, of this series vary but slightly: Methyl, 1.66; Ethyl, 1.69; Propyl, 1.66; *iso*-Propyl, 1.70; *tert*-Butyl, 1.66 Debyes (from the *Tables Annuelles*, 1937). It is probable that we are dealing with an essentially *three* centre problem, the resonances

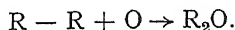


affecting the covalent molecule and the resonance $CH_3^+ \dots OH^-$, $OCH_3^- \dots H^+$ affecting the ions. Our theory is not competent to deal with so complex a situation. It is of great interest, however, that

²³ Baker and Nathan, *J. Chem. Soc.*, 1935, 1840.

²⁴ Wooster, *Chem. Rev.*, 1932, 11, 1-89.

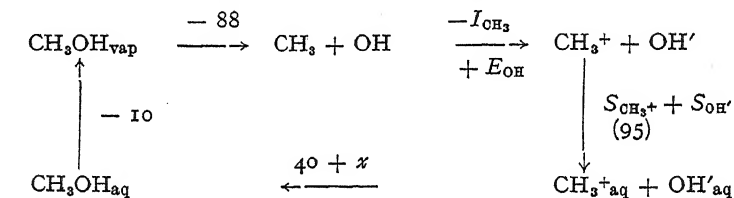
the average C—O bond strength in ethers seems to have practically the same value. Taking the I.C.T. values for the heats of combustion of methyl and ethyl ethers, and Rossini's values for the hydrocarbons, we can evaluate the heats of the processes:—



These, coupled with the appropriate C—C bond strengths from our earlier scheme,¹ yield for the average bond strength of C—O in dimethyl ether, 87.8 in diethyl ether 87.3. Unfortunately, there seem to be no combustion data for the higher aliphatic ethers. Since, however, the whole trend of this theory is to explain this constant value of 87 odd as due to a balance between several opposing effects, further data might help to clear up this situation.

APPENDIX.

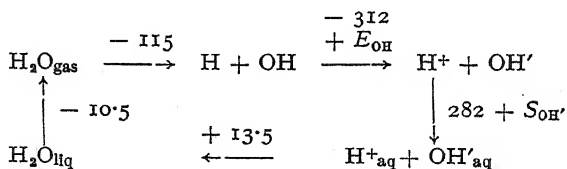
The ionisation potential of CH_3 can be "bracketed" by the two following methods: (1) It is known from the work of Polanyi and Szabo²⁵ that oxygen exchange between an alcohol and water containing the O_{18} isotope is slow, even at 100° , whence we may conclude $E > 40$ Cal. or so. Hence,



where $E = 40 + \pi$, π being positive.

$$\therefore O = \pi - I_{CH_3} + 37 + \{E_{OH} + S_{OH'}\} \quad (1)$$

The value for $S_{CH_3^+}$ has already been deduced, that for $CH_3OH_{aq} \rightarrow CH_3OH_{vap}$ comes from the known heats of solution and vaporisation of methyl alcohol, and the bond strength 88 from Table V. $E_{OH} + S_{OH'}$ can be obtained from the following cycle:—



(13.5 is the known heat of ionisation of water at 25°).

$$E_{OH} + S_{OH'} = 142 \quad (2)$$

It may be pointed out that as $S_{OH'}$ is probably about 107 (a calculated value due to Bernal and Fowler)¹⁰ $E_{OH} \simeq 35$. Lattice energy calculations on alkali metal hydroxides by Goubeau²⁶ gave a value 48 Cal.; earlier calculations by the same author gave the much higher value 76. It is

²⁵ Polanyi and Szabo, *Trans. Faraday Soc.*, 1934, 30, 508.

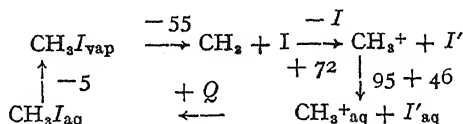
²⁶ Goubeau, *Z. physik. chem.*, B, 1936, 34, 432; Goubeau and Klemm, *ibid.*, 1937, 36, 362.

probable, therefore, that even the revised value is not very certain; a mean value $E \simeq 40$ may perhaps be recommended.

Hence, from (2) and (1)

$$I_{\text{CH}_3} = 180 + x \quad (3)$$

This gives a lower limit for the ionisation potential of methyl. A higher limit is obtained, since it is known from data on the rate of racemisation, hydrolysis, and isotopic exchange (from the work of Ingold)¹⁴ that alkyl halides show a tendency to ionise. This process requires an activation energy of the order 20 to 30 Cal., and we have justified the view that the heats of this reaction is practically the same. So, from this cycle



(the heat $\text{CH}_3\text{I}_{\text{v}} \rightarrow \text{CH}_3\text{I}_{\text{aq}}$ is unfortunately not known; 5 Cal. is a rough estimate)

$$0 = Q - 60 + 72 + 141 - I$$

$$Q = I - 153,$$

if

$$I = 180 + x$$

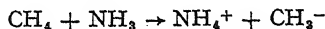
$$Q = 27 + x.$$

Hence the activation energy for the neutral solvolysis of CH_3I by water \simeq the heat of ionisation = $27 + x$. The experiments show x to be practically zero. Hence

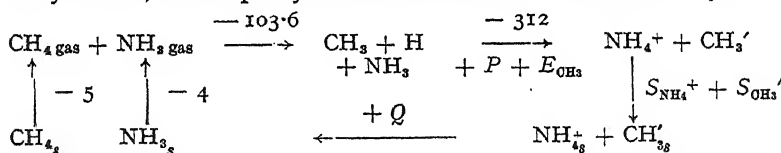
$$I_{\text{CH}_3} \simeq 180 \text{ Cal. (7.8 Volts),}$$

since a lower value would make difficulties about oxygen exchange, and a higher value would make difficulties for the ionic dissociation of methyl iodide. (The value of I for a free carbon atom is 11.2 Volts.)

The electron affinity of CH_3 can be estimated from the fact that the reaction



does not go to any marked extent in liquid ammonia. This reaction is fairly critical, since diphenyl methane does react. Consider the cycle



(the subscript "s" denotes the species in solution in liquid ammonia), where F is the proton affinity of NH_3 . Suppose $Q = 30 + x$ (x positive)

$$\therefore 0 = Q - 425 + P + E_{\text{OH}_3} + \{S_{\text{NH}_4^+} + S_{\text{CH}_3'}\}.$$

	<i>L.</i>	<i>H_s.</i>	<i>S.</i>	<i>S_{H₂O}.</i>
NH_4Cl	162	+ 6	168	158
NH_4Br	154	+ 8	162	152
NH_4I	146	+ 11	157	140

Table (*S* is the sum of the solvation heats of an ion and cation).

²⁷ Bleick, *J. Chem. Physics*, 1934, 2, 162.

²⁸ Kraus and Ridderhoff, *J.A.C.S.*, 1934, 56, 79.

The terms P (206 Cal.) and $S_{\text{NH}_4^+} + S_{\text{OH}_3'}$ can be evaluated from the data of Bleick²⁷ on the lattice energies L of ammonium salts, and the heats of solution H_s of ammonium salts in liquid ammonia measured by Kraus.²⁸ These data are shown in the

The heats of solvation in this solvent are larger than in water, although the solvent has a much lower dielectric constant; taking

$$S_{\text{NH}_4^+} + S_{\text{I}^-} \simeq S_{\text{NH}_4^+} + S_{\text{OH}_3},$$

from the approximate equality of the I^- and CH_3 radii already pointed out, $E_{\text{CH}_3} = 30 - x$. Similar cycles make it probable that x is about 10, whence

$$E_{\text{OH}_3} \simeq 20 \quad (6)$$

This is probably uncertain to at least ± 10 ; this will not, however, affect our previous conclusions to any significant extent, since $H_{11} - E$ is of the order 100-200 Cal. (The value for an unsubstituted carbon atom is uncertain as it depends on semi-empirical extrapolation of the ionisation potentials of *iso*-electronic atoms and ions. Thus Glockler²⁹ obtained 0.91 e.v. (21 Cal.) and Hellmann and Mamotenko³⁰ 1.37 e.v. (31 Cal.).

Summary.

The properties and electrolytic dissociation of bonds between (a) methyl and (b) hydrogen, halogen and sodium, are discussed in terms of the potential energy curves of the ground and ionic states of these bonds and their resulting ionic resonance energy. By considering also the additional resonance of alkyl radicals between several canonical forms, the observed bond strengths and dipole moment of some alkyl compounds are explained. Further applications are discussed.

²⁹ Glockler, *Physic. Rev.*, 1934, 46, III.

³⁰ Hellman and Mamotenko, *Acta physicochemica U.R.S.S.*, 1938, 7, 127; 1939, 8, 1.

³¹ *J. Amer. Chem. Soc.*, 1930 onwards, particularly Dorfman, *J.A.C.S.*, 1935, 57, 1455.

³² Whitmore, Wittle and Popkin, *J.A.C.S.*, 1939, 61, 1585.

THE INVESTIGATION BY ELECTRON DIFFRACTION OF THE STRUCTURES OF SOME TETRAHALIDES.

BY M. W. LISTER AND L. E. SUTTON.

Received 25th March, 1941.

It had been observed by several workers that the actual bond lengths in inorganic halides are frequently shorter than the sums of the covalent atomic radii such as are given by Pauling and Huggins.¹ Several explanations were put forward, but though each would account for some of the facts it seemed that no one would account for all of them. In the hope that a more complete knowledge of the facts would help in the choice of an explanation, we have examined as many as possible of the chlorides, bromides and iodides of the elements of group IV, and also selenium tetrachloride.

From what is known of the effective volumes of atoms it seemed likely that the valencies in certain tetrahalides would be stretched by the repulsion between halogen atoms,² and in order to test this possibility carbon tetrabromide and tetra-iodide were re-investigated.

¹ Pauling and Huggins, *Z. Krist.*, 1934, 87, 205.

² Sidgwick, *Ann. Repts. Chem. Soc.*, 1932, 29, 64.

Experimental.

Preparation and Purification of Materials.

Carbon tetrabromide.—A commercial specimen was purified by recrystallisation from alcohol, m.p. 92° . Von Barta³ gives m.p. 94° C.

Carbon tetra-iodide.—The method of preparation described by Durand⁴ was found to be unsatisfactory because, in the course of the repeated recrystallisations from benzene which it necessitated, a considerable amount of product was lost through oxidation by air.

The procedure described by Spindler,⁵ using CaI_2 on CCl_4 at 80° C. for 5 days in a sealed tube, was therefore employed. The product was purified by crystallisation from benzene in an atmosphere of CO_2 . Iodine was finally removed by washing with aqueous KI solution, followed by distilled water. The solid is quite stable in air at ordinary temperatures, and it is possible to heat it to 125° C. in the high vacuum of the electron diffraction apparatus without decomposition, though air oxidises it at a lower temperature.

Silicon tetrabromide.—Bromine in a stream of CO_2 was passed over silicon in a long Pyrex tube heated to $200\text{--}300^{\circ}$ C. Most of the unreacted bromine was removed from the product by distillation, and the last traces by Cu powder. The colourless liquid remaining was fractionally distilled and the middle fraction, b.p. 153° C., collected. Baxter, Weatherill and Scripture⁶ give b.p. 153° C.

Silicon tetra-iodide.—The method of preparation by direct union of the elements was attempted unsuccessfully, using Si prepared from SiO_2 and Al. It was, however, formed fairly easily by passing a slow stream of iodine vapour, carried along in CO_2 over magnesium silicide heated to bright redness in a Pyrex tube. (Gattermann⁷ used Si prepared from quartz sand and Mg, the active agent presumably being magnesium silicide.) The product was purified by dissolving it in dry CS_2 , removing free iodine by shaking with Hg, and evaporating the clear solution to dryness. The residue was recrystallised from CS_2 .

Germanium tetrabromide.—Finely divided germanium was prepared by reduction of the dioxide by a stream of hydrogen in a quartz tube at a very bright red heat. The bromide was prepared by passing a stream of bromine vapour in CO_2 over the germanium heated to $200\text{--}250^{\circ}$ C. Free bromine was removed from the product by distillation, and finally by copper bronze. The residue was distilled, the main fraction being collected directly in the tube in which it was used in the electron diffraction apparatus, m.p. 25.5° C. Dennis and Hance⁸ give m.p. 26.1° C.

Germanium tetra-iodide.—A specimen was provided by Mr. F. M. Brewer, m.p. 144.5° C. Dennis and Hance⁸ give m.p. 144° C.

Tin tetrabromide.—This substance was prepared by direct union of the elements, and purified by fractional distillation, m.p. 30° C. Melting points in the literature range from 29.5 to 33° C.

Tin tetra-iodide.—A commercial (Kahlbaum) specimen was used, m.p. 145.5° C. Reinders and de Lange¹⁰ give 143.5° C., but other and quite different values have also been given.

Lead tetrachloride.—Ammonium plumbichloride was precipitated by addition of aqueous NH_4Cl to a solution of chloroplumbic acid, formed by passing chlorine into a suspension of PbCl_2 in strong HCl. Lead tetra-

³ Von Barta, *Chem. Ztg.*, 1905, 29, 378.

⁴ Durand, *Bull. Soc. chim.*, 1927, 41 (4), 1251.

⁵ Spindler, *Annalen*, 1885, 231, 264.

⁶ Baxter, Weatherill, and Scripture, *Proc. Amer. Acad. Sci.*, 1923, 58, 245.

⁷ Gattermann, *Ber.*, 1889, 22, 190.

⁸ Dennis and Hance, *J. Amer. Chem. Soc.*, 1922, 44, 299.

⁹ *Idem.*, *ibid.*, 2854.

¹⁰ Reinders and de Lange, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 474.

chloride was prepared by stirring ammonium plumbichloride with excess of cold strong H_2SO_4 . The PbCl_4 which separates was washed with strong H_2SO_4 several times, and kept in a vacuum at room temperature for some time to remove free chlorine. This procedure does not remove all PbCl_2 which, however, is too involatile to matter.¹¹

Titanium tetrachloride.—This compound was prepared by direct union of the elements. A commercial specimen of Ti was mixed with some sugar charcoal to reduce any TiO present, and thus avoid the formation of the solid oxychloride, TiOCl_2 . The mixture was dried thoroughly at a red heat in a Pyrex tube in a slow stream of CO_2 . Chlorine was then passed over it, first at a low temperature, which was raised till the Ti ignited, and finally at a bright red heat. Chlorine was removed from the product by Cu powder, and the TiCl_4 distilled as a colourless liquid.

Titanium tetrabromide.—This also was prepared by direct union of the elements. Commercial Ti was as before mixed with sugar charcoal, and the whole, after thorough drying, heated to redness in a Pyrex tube through which passed a stream of bromine vapour carried over in CO_2 . The bromine was first dried by P_2O_5 . Most of the bromine was removed from the product by pumping off at room temperature. The TiBr_4 was then distilled into a tube containing Cu powder to remove the last traces of bromine, and thence distilled again to give yellow crystals, m.p. 37°C . Biltz and Keunecke¹² give m.p. 39°C .

Zirconium tetrachloride.—Metallic Zr was ignited in Cl_2 , and the product sublimed along a Pyrex tube. The most persistent impurity is FeCl_3 from Fe present in the zirconium. An unsuccessful attempt was made to remove it by reducing it to FeCl_2 through sublimation in hydrogen. Finally, as it is somewhat more volatile than zirconium chloride, it was removed by prolonged fractional sublimation.

Thorium tetrachloride.—This was prepared by the reaction between ThO_2 and CCl_4 ¹³ which was carried out with CCl_4 vapour at a bright red heat, and gave a sublimate of colourless crystals of ThCl_4 .

Selenium tetrachloride.—A commercial product was purified from SeOCl_2 , which is the chief impurity, by repeated fractional sublimation (or distillation of the more volatile SeOCl_2) up a long tube in a current of dry air.

Electron Diffraction Measurements.

The apparatus and technique used were those described previously.¹⁴

Carbon tetrabromide.—The photographs given by this substance showed seven or eight clearly marked maxima. The first two were very strong, after which a fairly regular diminution in intensity occurred, though the fifth maximum was about as strong as the fourth. All the maxima were symmetrical.

With this, as with all other tetrahalides of Group 4 elements which were examined, the appearance of the plate agreed perfectly with the theoretical curve for a tetrahedral model (see Figs. 1 and 2). Assuming this model, the interpretation of the plates becomes a one-parameter problem, and the following general treatment was applied. The theoretical curve and positions of the maxima are calculated for an arbitrary value (l) of the distance between the central and the halogen atoms. Each maximum then gives an observed distance for this link from the formula

$$l_{\text{true}} = l \cdot \frac{l_{\text{calc.}}}{l_{\text{obsd.}}}$$

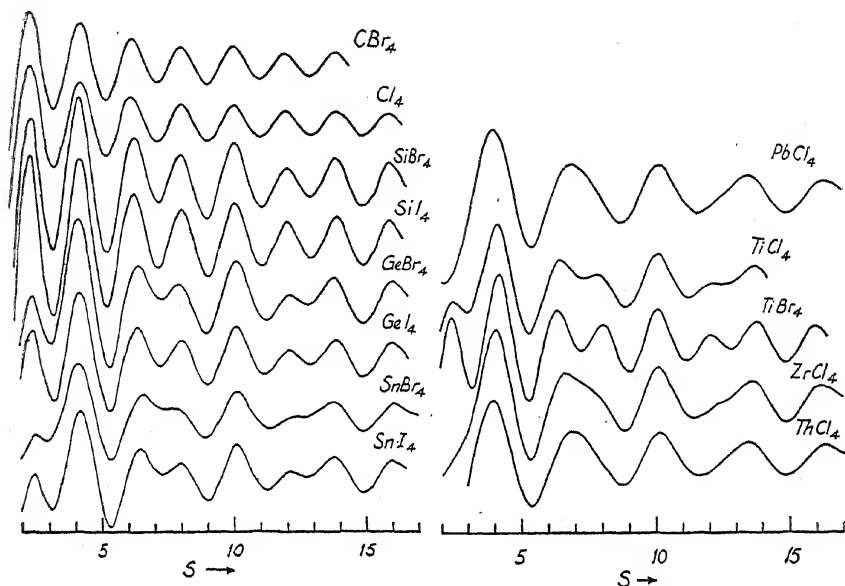
¹¹ Friedrich, *Ber.*, 1893, 26, 1434.

¹² Biltz and Keunecke, *Z. anorg. Chem.*, 1925, 147, 171.

¹³ Von Bolton, *Z. Elektrochem.*, 1908, 14, 768.

¹⁴ Lister and Sutton, *Trans. Faraday Soc.*, 1939, 35, 495.

where l_{true} is the observed distance, and $s_{\text{obsd.}}$ and $s_{\text{calc.}}$ are the observed and calculated $(4\pi \cdot \sin \theta/2)/\lambda$ values for any one maximum. The mean of the distances calculated from each maximum was taken as the final



FIGS. 1 AND 2.—Theoretical intensity curves for tetrahalides.

value, weighting each observed value according to the number of plates from which it was measured, and ignoring the first one or two maxima where these are too far in to be well measured, and ignoring also any extremely unsymmetrical maxima.

TABLE I.—CARBON TETRABROMIDE.

Max.	No. of Plates.	$s_{\text{obsd.}}$	$s_{\text{calc.}}$ C—Br = 2 Å.	$l_{\text{C—Br}}$ (Å).
1	6	2.48	2.38	(1.91)
2	6	4.44	4.29	1.932
3	6	6.45	6.28	1.949
4	6	8.43	8.13	1.928
5	6	10.42	10.10	1.940
6	6	12.40	12.03	1.939
7	5	14.36	13.91	1.937
8	2	16.31	15.90	1.949

Mean length of the C—Br link = 1.938 Å or 1.94 Å.

Average deviation = 0.005 Å.

$l_{\text{C—Br}} = 1.94 \pm 0.02$ Å.

The results for carbon tetrabromide are given in Table I.

Other measurements have been made on this compound. Lévy and Brockway¹⁵ have found C—Br = 1.91 \pm 0.02; de Laszlo¹⁶ 1.93 \pm 0.03; and Hassel and collaborators^{17, 18} 1.93 \pm 0.02.

The value now reported agrees well with that given

¹⁵ Lévy and Brockway, *J. Amer. Chem. Soc.*, 1937, 59, 1662.

¹⁶ De Laszlo, *Proc. Roy. Soc., A*, 1934, 146, 672.

¹⁷ Finbak and Hassel, *Z. physikal. Chem., B*, 1937, 36, 301.

¹⁸ Hassel and Sandbo, *ibid.*, B, 1938, 41, 75.

by the last-named authors although based only on the positions of maxima and not on those of maxima and minima.

Carbon tetra-iodide.—Twelve photographs were taken of this substance, the first six being over a range of temperature, and the last six at about 125° C.

There was no sign of decomposition at this temperature, either from the diffraction pattern observed, or from the appearance of the unsublimed residue in the oven. The plates showed from five to eight maxima, diminishing almost regularly in intensity from the centre outwards. The observed values of s at the maxima are given in Table II.

TABLE II.—CARBON TETRA-IODIDE.

Max.	No. of Plates.	$s_{\text{obsd.}}$	$s_{\text{calc. for C—I = 2 Å.}}$	$l_{\text{C—I (Å.)}}$
1	9	2.32	2.36	(2.04)
2	11	4.03	4.30	(2.13)
3	11	5.83	6.26	2.147
4	11	7.59	8.16	2.149
5	11	9.37	10.10	2.155
6	8	11.16	12.03	2.155
7	5	12.89	13.91	2.152
8	3	14.73	15.88	2.157

Mean length of the C—I link = 2.153 Å or 2.15 Å .

Average deviation = 0.003 Å .

$l_{\text{C—I}} = 2.15 \pm 0.02 \text{ Å}$.

This substance has also been examined by Finbak and Hassel¹⁷ who report $l_{\text{C—I}} = 2.12 \pm 0.02 \text{ Å}$ from photographs showing four maxima.

Silicon tetrabromide.—This substance gave from five to eight maxima, which were all well defined, closely spaced and symmetrical. The second maximum appeared rather stronger than the first, though both were very strong; then followed a moderately strong third maximum, a rather weaker minimum and a much weaker fourth maximum, then a stronger fifth, a faint sixth, and two slightly stronger and roughly equal maxima, the seventh and eighth. The observed s values are given in Table III.

TABLE III.—SILICON TETRABROMIDE.

Max.	No. of Plates.	$s_{\text{obsd.}}$	$s_{\text{calc. for Si—Br = 2 Å.}}$	$l_{\text{Si—Br (Å.)}}$
1	9	2.35	2.39	(2.03)
2	9	4.05	4.26	(2.11)
3	9	5.68	6.32	2.145
4	9	7.63	8.11	2.122
5	9	9.41	10.10	2.141
6	7	11.27	12.06	2.131
7	7	12.84	13.86	2.144
8	4	14.75	15.92	2.142

Mean length of the Si—Br link = 2.138 Å or 2.14 Å .

Average deviation = 0.007 Å .

$l_{\text{SiBr}} = 2.14 \pm 0.02 \text{ Å}$.

roughly equal intensity, as were the fourth and fifth, while the sixth was much weaker than the fifth. The observed values of s for the maxima are given in Table IV.

¹⁸ Wouters, de Hemptinne, and Capron, *Ann. Soc. sci. Bruxelles, B*, 1937, 57, 25.

Germanium tetrabromide.—The plates of this compound showed from five to eight maxima. The first maximum was very close in and rather weak, and was not measured. It was followed by a very strong maximum,

TABLE IV.—SILICON TETRA-IODIDE.

Max.	No. of Plates.	$s_{\text{obsd.}}$	$s_{\text{calc. for Si—I=2 Å.}}$	$l_{\text{Si—I. (Å.)}}$
1	II	2.00	2.38	(2.38)
2	II	3.53	4.26	2.41
3	II	5.18	6.30	2.432
4	II	6.72	8.12	2.415
5	II	8.31	10.10	2.433
6	IO	9.95	12.05	2.422
7	8	11.42	13.91	2.433
8	6	13.08	15.92	2.434

Mean value of the Si—I distance = 2.428 or 2.43 Å.

Average deviation = 0.006 Å.

$l_{\text{Si—I}} = 2.43 \pm 0.02$ Å.

a deep minimum and a moderately strong third maximum. The next minimum and maximum were weak, and the latter unsymmetrical, falling rapidly on the outside to a strong minimum. The fifth ring was strong, and was the most easily measurable and reliable ring on the plate. The sixth maximum was very weak, followed by two fairly weak

maxima separated by a deep minimum. The observed values of s are given in Table V.

The value obtained from the extremely unsymmetrical fourth maximum is ignored in the mean value of the bond length.

Rouault²⁰ reports that $l_{\text{Ge—Br}}$ in this compound is 2.32 Å.

Germanium tetra-iodide.—The plates of this substance showed from five to eight maxima. The first maximum was not very strong, and was followed by a very strong second maximum. The next minimum was very sharp; the third maximum fairly strong and quite sharp but followed, however, by a weak minimum. The fourth ring was much weaker and rather unsymmetrical. The fifth maximum was strong and symmetrical, falling between two deep minima. The sixth and seventh maxima were rather weak, and separated by a weak minimum, but were sharp and quite clearly measurable. After a deep minimum a weak eighth maximum was visible. The observed s values are given in Table VI.

TABLE V.—GERMANIUM TETRABROMIDE.

Max.	No. of Plates.	$s_{\text{obsd.}}$	$s_{\text{calc. for Ge—Br=2 Å.}}$	$l_{\text{Ge—Br (Å.)}}$
2	10	3.74	4.20	(2.24)
3	10	5.59	6.43	2.301
4	10	7.07	7.97	(2.25)
5	10	8.82	10.13	2.296
6	5	10.68	12.15	2.274
7	6	12.01	13.79	2.295
8	1	13.97	16.01	2.291

Mean length of Ge—Br link = 2.291 or 2.29 Å.

Average deviation = 0.007 Å.

$l_{\text{Ge—Br}} = 2.29 \pm 0.02$ Å.

Tin tetrabromide.—The plates of this substance showed from five to eight maxima. The first ring was weak and followed by a weak minimum. The second was very strong and symmetrical. The third maximum was fairly strong, followed by a weak minimum and an unsymmetrical weak fourth maximum. The fifth maximum was strong, symmetrical and very sharp. After a fairly strong minimum the sixth

²⁰ Rouault, C. R. *hebd. Seances Acad. Sci.*, 1938, 206, 51.

ring, though visible as a maximum, was little more than a shelf on the inside of the not very strong seventh maximum. The next minimum was sharp and followed by a rather weak eighth maximum. Owing to the unsymmetrical nature of the fourth and sixth maxima it was impossible to measure them reliably. The observed s values for the maxima are given in Table VII.

Tin tetra-iodide.

The plates of this substance all showed ten maxima. The general appearance of the plates was very similar to that of the germanium tetrabromide plates, though the fourth and sixth rings were relatively weaker. The latter maximum was not measured. After the eighth maximum another, the tenth, was visible and was relatively strong. The ninth ring was very weak and could not be measured. The s values observed for the maxima are given in Table VIII.

Lead tetrachloride.—It is difficult to get photographs of this substance as it is too unstable to give a large vapour pressure without appreciable decomposition. There is also a very large proportion of atomic scattering due to the lead atom relative to the molecular scattering, so that much background appears on the plates. Only one satisfactory plate was obtained, showing three rings. The s values for these rings were 3.38, 5.72 and 8.36. Assuming a tetrahedral model, the second and third maxima give values of 2.42 Å and 2.43 Å for the Pb—Cl distance. $l_{\text{Pb-Cl}} = 2.43 \pm 0.04$ Å.

Titanium tetrachloride.—The plates taken of this compound showed

TABLE VII.—TIN TETRABROMIDE.

Max.	No. of Plates.	$s_{\text{obsd.}}$	$s_{\text{calc. for Sn—Br}=2 \text{ Å.}}$	$l_{\text{Sn—Br (A).}}$
1	11	2.02	2.53	(2.50)
2	12	3.49	4.14	(2.37)
3	12	5.34	6.53	2.447
4	12	6.58	7.79	(2.37)
5	12	8.31	10.13	2.433
7	9	11.26	13.72	2.438
8	9	13.19	16.08	2.438

Mean value of Sn—Br distance = 2.439 or 2.44 Å.

Average deviation = 0.004 Å.

$l_{\text{Sn—Br}} = 2.44 \pm 0.02$ Å.

lowed by two weak and ill-separated rings, of which the further one (the seventh maximum) was the stronger. The s values for the maxima are given in Table IX.

TABLE VI.—GERMANIUM TETRA-IODIDE.

Max.	No. of Plates.	$s_{\text{obsd.}}$	$s_{\text{calc. for Ge—I}=2 \text{ Å.}}$	$l_{\text{Ge—I (A).}}$
1	10	1.95	2.41	(2.49)
2	10	3.44	4.22	(2.45)
3	10	5.06	6.37	2.516
4	10	6.47	8.06	2.489
5	10	8.08	10.10	2.501
6	8	9.70	12.09	2.492
7	8	10.96	13.84	2.525
8	5	12.82	15.96	2.490

Mean value of Ge—I distance = 2.502 or 2.50 Å.

Average deviation = 0.012 Å.

$l_{\text{Ge—I}} = 2.50 \pm 0.03$ Å.

from five to seven rings. The first was weak and the second very strong followed by a deep minimum. The third was less strong but sharp, and followed by a weak minimum separating it from the unsymmetrical and weak fourth maximum. Then came a strong symmetrical fifth maximum rising between two deep minima, and fol-

Titanium tetrabromide.—The plates of this substance showed seven or usually eight rings, and were very similar in appearance to those obtained from germanium tetra-iodide, which have already been described.

TABLE VIII.—TIN TETRA-IODIDE.

Max.	No. of Plates.	$s_{\text{obsd.}}$	$s_{\text{calc. for Sn—I = 2 \text{ \AA.}}}$	$l_{\text{Sn—I (A.)}}$
1	10	1.85	2.44	(2.65)
2	11	3.23	4.18	(2.59)
3	12	4.89	6.43	2.632
4	11	6.09	7.97	2.614
5	12	7.65	10.13	2.647
7	12	10.34	13.79	2.666
8	12	12.21	16.01	2.621
10	12	14.66	19.69	2.686

Mean value of Sn—I distance = 2.64 Å.

Average deviation = 0.02 Å.

$l_{\text{Sn—I}} = 2.64 \pm 0.04$ Å.

TABLE IX.—TITANIUM TETRACHLORIDE.

Max.	No. of Plates.	$s_{\text{obsd.}}$	$s_{\text{calc. for Ti—Cl = 2 \text{ \AA.}}}$	$l_{\text{Ti—Cl (A.)}}$
1	8	2.30	2.51	2.186
2	8	3.85	4.16	2.163
3	8	5.88	6.50	2.212
4	8	7.34	7.84	2.137
5	8	9.27	10.13	2.184
6	6	11.18	12.34	2.207
7	7	12.49	13.73	2.197

Mean length of the Ti—Cl link = 2.18 Å.

Average deviation = 0.02 Å.

$l_{\text{Ti—Cl}} = 2.18 \pm 0.04$ Å.

TABLE X.—TITANIUM TETRABROMIDE.

Max.	No. of Plates.	$s_{\text{obsd.}}$	$s_{\text{calc. for Ti—Br = 2 \text{ \AA.}}}$	$l_{\text{Ti—Br (A.)}}$
1	6	2.10	2.41	2.305
2	6	3.68	4.22	2.294
3	6	5.49	6.37	2.320
4	6	6.95	8.06	2.318
5	6	8.74	10.10	2.313
6	6	10.47	12.09	2.310
7	6	11.88	13.84	2.331
8	5	13.85	15.97	2.306

Mean length of Ti—Br bond = 2.312 or 2.31 Å.

Average deviation = 0.008 Å.

$l_{\text{Ti—Br}} = 2.31 \pm 0.02$ Å.

The s values for the maxima are given in Table X.

Zirconium tetrachloride.—This compound gave plates with five rings. The first of these was strong with a deep minimum outside. The second was much less intense than the first, and was unsymmetrical, falling slowly to something of a shelf on the outside. The third maximum was relatively strong and was very sharp. Outside it was a broad minimum, followed by two progressively weaker rings separated by a sharp minimum. The s values for the maxima are given in Table XI.

Thorium tetrachloride.—Thorium chloride did not easily give good photographs, as, apart from the high temperature needed to volatilise it (550–600° C.), there is much atomic scattering due to the heavy thorium atom. The plates showed up to five rings, all fairly symmetrical. The fall of the second ring, steeper on the inside than the outside, was visible on the plates. The observed s values of the maxima are given in Table XII.

Selenium tetra-

chloride.—The plates of selenium tetrachloride showed up to five regularly spaced maxima, and Table XIII gives the observed s values together with the distances to which they correspond on both a planar and a tetrahedral model (see Fig. 3).

The average deviations favour the tetrahedral model, but the evidence is not decisive. In view of the observations made by Schomaker and Stevenson on tellurium tetrachloride,²¹ it is probable that neither of these models is quite correct; since, however, the Se—Cl bond-length is but little affected by the model no others were tried. The probable length of the Se—Cl bond is 2.13 ± 0.04 Å. The theoretical scattering curves for the two models are shown in Fig. 3.

TABLE XI.—ZIRCONIUM TETRACHLORIDE.

Max.	No. of Plates.	$s_{\text{obsd.}}$	$s_{\text{calc. for Zr—Cl}=2 \text{ Å.}}$	$l_{\text{Zr—Cl. (Å.)}}$
1	7	3.59	4.07	(2.27)
2	8	5.59	6.70	2.396
3	7	8.76	10.13	2.314
4	7	11.61	13.62	2.347
5	7	14.17	16.20	2.285

Mean length of the Zr—Cl link = $2.33(5)$ Å.

Average deviation = 0.03 Å.

$l_{\text{Zr—Cl}} = 2.33(5) \pm 0.05$ Å.

TABLE XII.—THORIUM TETRACHLORIDE.

Max.	No. of Plates.	$s_{\text{obsd.}}$	$s_{\text{calc. for Th—Cl}=2 \text{ Å.}}$	$l_{\text{Th—Cl. (Å.)}}$
1	5	3.23	4.00	(2.48)
2	5	5.29	6.92	2.615
3	4	7.83	10.17	2.597
4	4	10.23	13.48	2.636
5	3	12.54	16.36	2.608

Mean length of the Th—Cl link = 2.614 or 2.61 Å.

Average deviation = 0.011 Å.

$l_{\text{Th—Cl}} = 2.61 \pm 0.03$ Å.

TABLE XIII.

Max.	Min.	No of Plates.	s .	$l_{\text{Se—Cl.}}$	
				Planar.	Tetrahd.
1		10	3.88	(1.89)	2.130
	2	12	5.37	2.141	(2.00)
2		12	6.38	2.200	2.078
	3	11	8.29	2.066	2.142
3		12	9.53	2.076	2.127
	4	6	11.01	2.192	2.071
4		10	12.39	2.178	2.205
	5	—	—	—	—
5		4	15.22	2.139	2.122
			Average	2.142	2.125
			Average deviation	0.041	0.030

²¹ Schomaker and Stevenson, *J. Amer. Chem. Soc.*, 1940, **62**, 1270.

Discussion.

As may be seen from Table XIV below, carbon tetra-iodide and tetra-bromide are alone among the Group IV tetrahalides examined in having bond distances greater than the radius sums. The difference of $+0.05$ Å which we find for the former is probably outside the experimental error, and while that of $+0.03$ Å for the tetrabromide could be attributed to error if it were by itself, the case of the iodide suggests that it is real.

The energy necessary to stretch four C—I bonds by 0.05 Å each is at most only 1.65 k.cal./g. mol.* In carbon tetra-iodide there must also be the energy necessary to compress the unbonded iodine atoms along the six tetrahedral edges; but the total stereochemical destabilisation is unlikely to be more than 5 k.cal./g. mol. It therefore appears that this is not the primary cause of the instability of carbon tetra-iodide, e.g., towards oxidation (p. 394). In iodoform the heat of formation Q_a of the C—I bond is found to be 40.6 k.cal./g. mol.†; and if it were the same in carbon tetra-iodide the heat of formation of this substance relative to the constituent elements in their standard states Q_f would be -64 k.cal./g. mol. Thus, the relative weakness of the C—I bond is sufficient to make the molecule unstable (Q_f for nitrogen trichloride is -55), and the further effect of steric destabilisation is not very important.

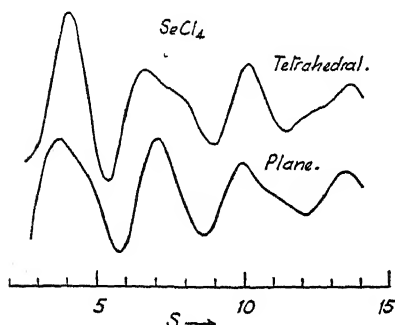


FIG. 3.—Theoretical curves for plane and tetrahedral models of selenium tetrachloride.

iodide, methylene iodide, and in iodoform are 39.8 , 40.0 and 40.6 k.cal./g. mol. and so are equal within the experimental error, indicating the absence of any appreciable repulsion energy in the two latter over and above what there may be in the first owing to repulsion between the hydrogen and iodine atoms. This is probably because of the relative ease with which the strain can be relieved by change of valency angle.

The length found for the Se—Cl bond in selenium tetrachloride is of interest in that it agrees exactly with the value calculated for it from the tetrahedral selenium radius ascribed by Pauling and Huggins, the

* This is the energy value if the stretching force-constant, k_{C-I} , for the bonds is $2.3 \cdot 10^5$ dynes/cm. as it is in methyl iodide.²² It is probably less,^{22a} so this energy value is a maximum.

²² (a) Sutherland, *Trans. Faraday Soc.*, 1938, **34**, 325; (b) Linnett, *J. Chem. Physics*, 1940, **8**, 91.

† The thermochemical data are from Bichowsky and Rossini, *The Thermochemistry of Chemical Substances*, New York, 1936; and Q_a values are for the formation of the substances in the gas phase from the atoms. The heat of atomisation of carbon is taken as 124 k.cal./g. mol.²³

²³ Herzberg, *Chem. Reviews*, 1937, **20**, 145.

observed and calculated values being 2.13 ± 0.04 Å and 2.13 Å respectively. Other authors have reported a similar agreement for the Te—Cl bond in tellurium tetrachloride.²¹

TABLE XIV.

Table XIV summarises the data for tetrahalides of Group IV elements:—

The radii used for titanium and zirconium are 1.28 and 1.42 Å respectively, which values were obtained by multiplying the octahedral radii, 1.36 and 1.51 Å,¹ into the ratio value of 0.943 found for the tetrahedral to octahedral radii in tin and lead compounds. The thorium radius used was 1.68 Å, and it was obtained by extrapolation from the silicon, titanium, and zirconium values, assuming that the approximately constant increase in this series continues; it is probably not very accurate.

If the results for Group IV tetrahalides be considered together with those for the normal halides of the

previous Groups, the trihalides of Group V, and the dihalides of Group VI,* certain trends in the percentage differences become apparent, some

Group IV Element.		Halogen.	F.	Cl.	Br.	I.
C	obsd.	.	1.36*	1.76*	1.94†	2.15
	calc.	.	1.41	1.76	1.91	2.10
	diff.	.	-0.05	0	+0.03	+0.05
	%	.	-3.5	0	+1.6	+2.4
Si	obsd.	.	1.54*	2.00*	2.15	2.43
	calc.	.	1.81	2.16	2.31	2.50
	diff.	.	-0.27	-0.16	-0.16	-0.07
	%	.	-14.9	-7.4	-6.9	-2.8
Ti	obsd.	.	—	2.18	2.31	—
	calc.	.	—	2.27	2.42	—
	diff.	.	—	-0.09	-0.11	—
	%	.	—	-4.0	-4.5	—
Zr	obsd.	.	—	2.33(5)	—	—
	calc.	.	—	2.41	—	—
	diff.	.	—	-0.07(5)	—	—
	%	.	—	-3.1	—	—
Th	obsd.	.	—	2.61	—	—
	calc.	.	—	2.67	—	—
	diff.	.	—	-0.06	—	—
	%	.	—	-2.2	—	—
Ge	.	.	—	2.08*	2.29	2.50
	.	.	—	2.21	2.36	2.55
	.	.	—	-0.13	-0.07	-0.05
	.	.	—	-5.9	-3.0	-2.0
Sn	.	.	—	2.30*	2.44	2.64
	.	.	—	2.39	2.54	2.73
	.	.	—	-0.09	-0.10	-0.09
	.	.	—	-3.8	-3.9	-3.3
Pb	.	.	—	2.43	—	—
	.	.	—	2.45	—	—
	.	.	—	-0.02	—	—
	.	.	—	-0.8	—	—

* References 27, 28.

† Present work and reference 15.

* In TeCl_2 , $l_{\text{TeCl}} = 2.36 \pm 0.03$ obsd., $l_{\text{calc.}} = 2.36$;

in TeBr_2 , $l_{\text{TeBr}} = 2.49 \pm 0.03$ obsd., $l_{\text{calc.}} = 2.51$;

hence there is no significant departure from additivity in either compound.²⁴

²⁴ Grether, *Ann. Physik.*, 1936, 26, 1.

of which have been noted and discussed elsewhere. These data are assembled together in Table XV.

Relatively few of the bonds are normal in length, within the 1 % which is the probable experimental error for many of the figures. Most of the bonds are short, although a few are long. The increases of length in Group IV have already been discussed; some of those in Group V are less certain, because, in the examination of the trihalides, it is necessary to evaluate the angle as well as the bond length. § This is not true of the increase in the N—Cl bond, which is observed in the compounds $(\text{CH}_3)_2\text{NCl}$ and CH_3NCl_2 ³³ and which can be taken as well-established. Those in Groups VI and VII also are certainly real.

In Groups IV, V, and VI the contractions follow three general rules:—

(1) They fall steadily from fluoride to iodide, *i.e.*, the observed distances approximate more closely to the sums of the radii in this order.

(2) In a series of compounds with the same halogen attached to the different elements of one Group, the shortening is less the later the Period of the element, save for the First Period. No carbon compound exhibits a contraction (except the tetrafluoride), the boron compounds show very large ones, while the halides of nitrogen, oxygen, and fluorine have elongated bonds.

(3) In a series of compounds where the same halogen is attached successively to the elements of one Period, the shortening is less the later the Group of the element.

There are some exceptions to the first and second rules, although some of the divergences are within the probable experimental error. To rule (1) the pair Ti—Cl and Ti—Br is a possible exception; to rule (2) the pairs Ge—Br and Sn—Br, Ge—I and Sn—I are probable exceptions, while P—I, As—I and Sb—I are possible exceptions. Rule (2) certainly applies, however, to all chlorides, with the over-riding exclusion, noted above, of those of elements in the First Short Period.

The contractions in the Group II and Group III halides do not follow rule (1): instead they are much the same for chlorides, bromides, and iodides, while that for the one fluoride examined is much greater. Rule (2) appears to apply to the cadmium halides as compared with the mercuric ones. Rule (3) cannot be applied in comparing compounds of Group II and Group III with each other because the data are too scanty, but it holds if compounds in either of them are compared with those in the later Groups.

§ Several estimates of error given in the paper by Gregg, Hampson, G. I. Jenkins, P. L. F. Jones, and Sutton²⁶ are too small because proper account was not taken of this. Considering both uncertainty of angle and deviations from the average distance value for any one angle, the revised values are:—

$l_{\text{PBr}} = 2.23 \pm 0.04$;	$l_{\text{SbCl}} = 2.37 \pm 0.02$;
$l_{\text{PI}} = 2.52 \pm 0.07$;	$l_{\text{SbBr}} = 2.52 \pm 0.03$;
$l_{\text{AsBr}} = 2.36 \pm 0.04$;	$l_{\text{SbI}} = 2.75 \pm 0.05$.
$l_{\text{AsI}} = 2.58 \pm 0.05$.	

²⁵ (a) Lévy and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 2085; (b) Braune and Pinow, *Z. physikal. Chem.*, B, 1937, **35**, 239.

²⁶ Gregg, Hampson, G. I. Jenkins, Jones, and Sutton, *Trans. Faraday Soc.*, 1937, **33**, 852.

²⁷ Brockway and H. O. Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036.

²⁸ Brockway, *Rev. Mod. Physics*, 1936, **8**, 231.

²⁹ Hassel and Strømme, *Z. physikal. Chem.*, B, 1938, **38**, 466.

³⁰ Brockway, *J. Amer. Chem. Soc.*, 1938, **60**, 1348.

Several explanations of the contractions have been proposed^{25(a), 26, 27, 34, 35} and recently the elongations have been included.^{36, 37} The data have now been augmented by these new measurements on tetrahalides, by others on trihalides and pentahalides,^{32, 38} as well as by observations on the mixed methyl-halogen derivatives of tin, arsenic, and nitrogen.^{33, 39} As will be shown in a later paper (see also³⁷) a careful examination of the facts now available makes it difficult to accept any one of the early explanations as satisfactory and sufficient; and supports the suggestion made by Gregg and his collaborators,²⁶ that there may be several causes in operation with different relative importance according to the Group of the central atom.

TABLE XV.

Group. Period.	II.	III.		IV.				V.				VI.		VII.
I		F.	Br.	F.	Cl.	Br.	I.	F.	Cl.	Br.	I.	F.	Cl.	F.
II		B	—	C	—	—	—	N	—	—	—	O	—	—
		—	—	Si	—	—	—	P	—	—	—	S	—	—
		—15.0*	—8.0*	—14.9†	—7.4†	—6.9	—2.0	—12.6†	—4.3†	—0.4	—3.7	—8.5†	+1.8†	+13.3‡
		—	—	—	—	—	—	—	—	—	—	—	—	—
III														
IV														
V														
VI														

* References 25, 26. These percentages are based on the tetrahedral radius of 0.89 Å for boron (see ref. 25(a)); if the trivalent radius of 0.79 Å be taken as the basis the corresponding values are -9.1, 2.8, and +3.1%.

† Reference 29. The tetrahedral radius is used for zinc.¹ For mercury the tetrahedral radius proves to be identical with the normal valent one.^{24, 27}

‡ Reference 30.

§ Reference 31.

|| Reference 32.

¶ Reference 33.

‡‡ Reference 34.

§§ Reference 35(b), 26.

Summary.

The structures of a number of tetrahalides have been determined from the scattering of fast electrons by their vapours. In every case where the configuration would have an important effect upon the mode of scattering it was found that the assumption of a tetrahedral molecule was entirely satisfactory. A different configuration might be expected for selenium tetrachloride, but the photographs obtained did not allow of a decision being made.

The bond lengths found were (in Å):—

$l_{\text{C-Br}} = 1.94 \pm 0.02$;	$l_{\text{C-I}} = 2.15 \pm 0.02$;
$l_{\text{Si-Br}} = 2.14 \pm 0.02$;	$l_{\text{Si-I}} = 2.43 \pm 0.02$;
$l_{\text{Ge-Br}} = 2.29 \pm 0.02$;	$l_{\text{Ge-I}} = 2.50 \pm 0.03$;
$l_{\text{Sn-Br}} = 2.44 \pm 0.02$;	$l_{\text{Sn-I}} = 2.64 \pm 0.04$;
$l_{\text{Pb-Cl}} = 2.43 \pm 0.04$;	$l_{\text{Ti-Br}} = 2.31 \pm 0.02$;
$l_{\text{Ti-Cl}} = 2.18 \pm 0.04$;	$l_{\text{Th-Cl}} = 2.61 \pm 0.03$;
$l_{\text{Zr-Cl}} = 2.33(5) \pm 0.05$;	$l_{\text{Se-Cl}} = 2.13 \pm 0.04$.

These measurements provide a number of further examples of bonds which are shorter than the sums of the covalent radii ascribed by Pauling and Huggins. Coupled with earlier measurements, they emphasise the fact that the percentage contractions in the halides of the elements of Groups II and III obey different rules from those which apply to the contractions in halides of elements in Groups IV—VII; and they therefore support the contention that there are at least two factors responsible for the contractions.

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THE INVESTIGATION BY ELECTRON DIFFRACTION OF SOME DIHALIDES OF CADMIUM, TIN AND LEAD.

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In extension of the work described in the previous paper we have examined a number of dihalides. Some are of a metal with a group valency of two, *viz.*, cadmium; and some are of metals which display di-valency because of the operation of the "inert pair" effect, *viz.*, tin and lead.

The two classes of dihalide were expected to show a difference in valency angle, for although in the cadmium compounds this should be 180° as it is in the mercuric compounds,^{1, 2, 3, 4, 5} in the others it

¹ Krishnamurti, *Ind. J. Physics*, 1930, **5**, 113.

² Braune and Engelbrecht, *Z. physikal. Chem.*, B, 1930, **10**, 1; *ibid.*, 1931, **11**, 409.

³ Braune and Knoke, *ibid.*, 1933, **23**, 163.

⁴ Braune and Linke, *ibid.*, 1935, **31**, 12.

⁵ Gregg, Hampson, G. I. Jenkins, P. L. F. Jones, and Sutton, *Trans. Faraday Soc.*, 1937, **33**, 870.

would be expected to be nearer 90° , both from theory and from measurements on related compounds.⁶ As will be explained in the experimental section, however, it was found impossible to determine the angle in the tin and lead compounds because of the effects of temperature on the diffraction pattern. Such effects have been considered theoretically by James,⁷ and have been considered in the instance of tetranitromethane,⁸ but appear not to have been previously observed for such simple compounds in electron diffraction experiments.

Experimental.

Preparation and Purification of Materials.

Stannous chloride.—Hydrated crystals of this substance were dehydrated by heating and finally distilling them in a stream of HCl.

Stannous bromide.—Tin was dissolved in aqueous HBr, and the solution evaporated to give crystals of the hydrated salt, which were treated in a manner similar to that for SnCl_2 .

Stannous iodide.— SnI_2 was precipitated by the double decomposition of SnCl_2 (1 mol.), KI (2 mols.) in the presence of HCl (1 mol.) in hot strong aqueous solution. According to Freundler and Laurent⁹ at temperatures above 50°C . the precipitate consists of anhydrous SnI_2 . The product was filtered off, dried, and finally sublimed in a stream of CO_2 to prevent oxidation by air.

Plumbous chloride, bromide and iodide.—These were all prepared by precipitation by double decomposition in aqueous solution, and were recrystallized from water.

Cadmium chloride and bromide.—These were prepared by dissolving the oxide in HCl or HBr and evaporation to dryness. They were dried by heating and subsequent distillation in a Pyrex tube, a slow stream of N_2 being used to carry away the water, and finally to take the vapour of the distilling salt along the tube. Even though the dehydration was carried out in N_2 and not in HCl or HBr, there appeared to be very little hydrolysis.

Cadmium iodide.—A commercial (Kahlbaum) specimen was used.

Electron Diffraction.

The apparatus and general experimental technique employed were those described previously.¹⁰

TABLE I.—STANNOUS CHLORIDE.

Max.	Min.	No. of Plates.	$s_{\text{obsd.}}$	
1		6	3.28	
	2	6		4.61
2		6	5.81	
	3	6		7.09
3		6	8.48	
	4	6		9.69
4		6	11.05	
	5	5		12.19
5		6	13.45	

Results.

Stannous chloride.—The plates obtained from this substance showed five rings, which were all fairly symmetrical, and fell fairly uniformly in intensity from the centre outwards. The s values ($= 4\pi \sin \frac{\theta}{2} / \lambda$) observed for the maxima and minima are given in Table I.

The interpretation of the plates obtained from stannous chloride, bromide and iodide will be discussed together.

⁶ Powell and Tasker, *J. Chem. Soc.*, 1937, 119.

⁷ James, *Physikal. Z.*, 1932, 33, 737.

⁸ Stosick, *J. Amer. Chem. Soc.*, 1939, 61, 1127.

⁹ Freundler and Laurent, *Bull. Soc. chim.*, 1925 (4), 37, 1133.

¹⁰ Lister and Sutton, *Trans. Faraday Soc.*, 1939, 35, 495.

Stannous bromide.—This compound gave plates with up to six rings, which were all symmetrical and whose intensities fell off fairly regularly

TABLE II.—STANNOUS BROMIDE.

Max.	Min.	No. of Plates.	$s_{\text{obsd.}}$
1		13	3.20
	2	6	4.46
2		14	5.49
	3	6	6.85
3		14	8.03
	4	6	9.41
4		13	10.46
	5	9	11.86
5		9	12.99
	6	—	—
6		1	15.34

TABLE III.—STANNOUS IODIDE.

Max.	Min.	No. of Plates.	$s_{\text{obsd.}}$
1		6	2.85
	2	6	4.12
2		6	5.13
	3	6	6.35
3		6	7.48
	4	6	8.63
4		6	9.75
	5	6	10.92
5		6	12.13

from the centre. The observed values of s for the maxima and minima are given in Table II.

Stannous iodide.—Five maxima were observed for stannous iodide. These were all symmetrical and regularly spaced, and fell off fairly regularly in intensity. The minima were also symmetrical and of steadily decreasing depth. The s values observed for the maxima and minima were :—

The first question which arises in the interpretation of these plates

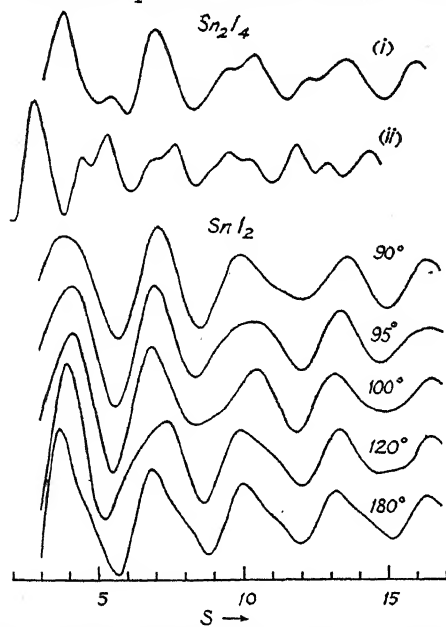
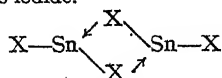


FIG. 1.—Theoretical intensity curves for various models of stannous iodide.

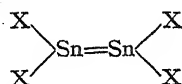


is the molecular formula of the diffracting vapour; that is, whether it is SnX_2 or Sn_2X_4 . Biltz and Meyer's results for the vapour density of stannous chloride¹¹ indicate that at the temperature and pressure of diffraction there would be very little if any association. The pressure of the diffracting vapour is certainly not above 5 mm. of mercury, which is the vapour pressure in the oven found to give the best results, and will be very considerably below this when it has diffused through the capillary jet of the oven head into the high vacuum of the camera. To confirm this, however, theoretical curves for Sn_2X_4 were calculated, assuming the following models :—

(i) A regular planar model of the form

¹¹Biltz and Meyer, *Z. physikal. Chem.*, 1888, 2, 184.

(ii) A regular planar model of the form



These curves are plotted in Fig. 1, and bear no resemblance to the appearance of the plate.

If, therefore, the molecular formulæ are taken as SnX_2 , two independent variables must be determined in order to fix the structure: namely, the

TABLE IV.— SnI_2 .

Angle Max.	90°.	95°.	100°.	110°.	120°.	150°.	180°.
2	2.768	2.721	2.682	2.639	2.849	2.705	2.678
3	2.647	2.733	2.786	2.706	2.647	2.722	2.679
4	2.774	2.732	2.688	2.784	2.723	2.746	2.682
5	2.688	2.718	2.750	2.684	2.739	2.737	2.688
Mean	2.712	2.726	2.726	2.703	2.739	2.728	2.682 A
Average deviation	0.049	0.006	0.041	0.042	0.054	0.014	0.003

length of the Sn—X bond, and the tin valency angle. The procedure first adopted was to calculate curves for models with an arbitrary Sn—X distance of 2 Å, and various X—Sn—X angles. Then for any curve an observed value can be calculated for the Sn—X distance from each maximum, and that model is finally chosen which shows the least average deviation amongst the Sn—X distances so obtained. This method can be most advantageously applied to stannous iodide, for here the halogen-halogen term which is dependent on the valency angle is most important relative to the tin-halogen term.

Fig. 1 shows the theoretical curves for stannous iodide for various angles. The Sn—I distances calculated from various models are given in Table IV.

Thus there are two angles, 95° and 180°, which give theoretical curves whose maxima fit the observed ones with an accuracy as great as is the accuracy of observation of the maxima. On quantitative grounds it

is impossible to select one or other. The curve for 180° is, however, shaped like a saw edge, and a plate with such a curve would be almost identical with those obtained from cadmium iodide (*q.v.*), where the angle is 180°. On these latter plates the unsymmetrical nature of the maxima is most marked and quite unmistakeable; the stannous iodide plates

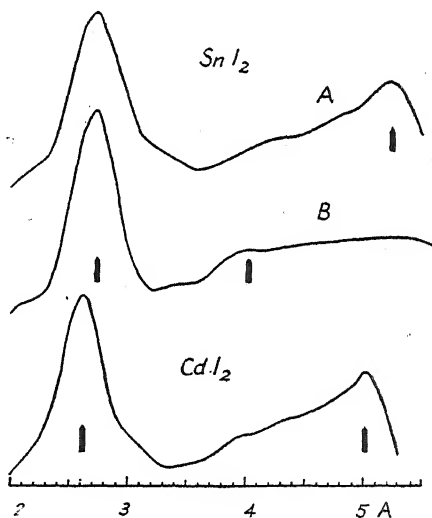


FIG. 2.—Radial distribution curves for stannous iodide and cadmium iodide.

show no such asymmetry, so that the model with an I—Sn—I angle of 180° can be rejected. This leaves the angle as 95° . A similar conclusion is reached from the radial distribution curves of the older kind ¹² (Fig. 2, A and B). A shows the result when maxima only are taken into account ;

Halogen.	I _{Sn} —X in Å.
Cl	2.42 ± 0.02
Br	2.55 ± 0.02
I	2.73 ± 0.02

it indicates distances of 2.73 and 5.24 (shown by heavy arrows), *i.e.*, an angle of nearly 180° ; while B shows the effect of including minima as well ; it indicates an angle of 95° .

Minima of deviation at 95° and 180° were also found with the other stannous halides and with the plumbous halides, but, as we shall see later (p. 411), this proves not to be a convincing reason for thinking that the angle really is 95° .

However, our immediate need is to know what we may call the *apparent* configurations which will enable us to calculate the bond lengths accurately, and it will be shown that the 95° configurations are satisfactory for this purpose in all these dihalides. The bond lengths then obtained for the stannous halides are shown in table above.

Plumbous chloride.—This compound has a very unfavourable ratio of molecular to atomic scattering. Plates were obtained with four rings, which were symmetrical and fell off regularly from the centre. The *s* values observed for the maxima and minima are given in Table V.

The interpretation of the plates of the three plumbous halides examined will be discussed together.

Plumbous bromide.—The plates from this compound showed five symmetrical maxima, whose intensities fell off regularly from the centre. The *s* values observed for the maxima and minima are given in Table VI.

TABLE V.—PLUMBOUS CHLORIDE.

Max.	Min.	No. of Plates.	<i>s</i> _{obsd.}
1		6	3.38
	2	5	4.51
2		6	5.69
	3	5	7.07
3		6	8.27
	4	2	9.40
4		3	10.82

TABLE VII.—PLUMBOUS IODIDE.

Max.	Min.	No. of Plates.	<i>s</i> _{obsd.}
1		6	2.98
	2	6	4.02
2		6	5.05
	3	6	6.11
3		6	7.31
	4	6	8.48
4		6	9.55
	5	6	10.72
5		6	11.82
	6	6	12.87
6		5	13.96

TABLE VI.—PLUMBOUS BROMIDE.

Max.	Min.	No. of Plates.	<i>s</i> _{obsd.}
1		3	3.19
	2	4	4.35
2		4	5.45
	3	4	6.70
3		4	7.84
	4	4	9.17
4		4	10.19
	5	3	11.47
5		3	12.57

Plumbous iodide.—Six rings were obtained with this compound, all of which were symmetrical and of regularly decreasing intensity from the centre outwards, and were situated at the *s* values given in Table VII.

¹² Brockway, *Rev. Mod. Phys.*, 1936, 8, 231.

For an apparent angle of 95° , the bond-lengths calculated for the plumbous halides are the following :—

The Temperature Effect.

As was stated previously, if for any of the stannous or plumbous halides the average deviations of bond length are plotted against the assumed valency angle, sharp minima are obtained at 95° and 180° . The qualitative agreement between the appearance of the plates and the shape of the theoretical curves for 180° is not good when the halogen-halogen terms are relatively important, but neither is that with the 95° curves. Thus the 95° curve for stannous iodide gives the first and second maxima nearly equal intensities, and likewise the third and fourth, yet the intensities of the actual maxima fall off steadily; furthermore, the quantitative fit of the minima is not very good.

Now, an angle of 95° makes the halogen-halogen distance nearly 1.5 times the metal-halogen distance, and hence the maxima of the theoretical curve approximate more closely than for any other angle except 180° to those of a simple $\sin s/l$ curve; the maxima of the metal-halogen term coincide alternately with a maximum and a minimum of the halogen-halogen term.

All the observed maxima and minima would fit a $\sin s/l$ curve well; e.g., the *minima* for stannous iodide with such a curve give :—

Min.	2.	3.	4.	5.	Mean.	Av. Dev.
$l_{\text{Sn-I}}$	(2.65)	2.713	2.725	2.731	2.723	0.007 A.

whereas the values calculated from a 95° model show considerably more variation :—

Min.	2.	3.	4.	5.	Mean.	Av. Dev.
$l_{\text{Sn-I}}$	(2.728)	2.630	2.765	2.689	2.695	0.047 A.

An explanation which therefore appears possible is that the thermal vibration of the molecule makes the halogen-halogen terms less distinct and important than was anticipated. James⁷ has shown that, for the diffraction of X-rays by vapours, if $\overline{\delta l_{ij}^2}$ is the mean square deviation of l_{ij} owing to vibration, then the coherent term in the theoretical expression for the diffracted intensity must be multiplied by $e^{-(\overline{\delta l_{ij}^2} \cdot s^2)/2}$. This same result should hold for electron diffraction.¹² In general it is found that the bending of two valencies relative to each other is easy compared with the stretching of a link, and so the importance of the halogen-halogen term will be decreased relative to the metal-halogen term. The force-constants of the stannous and plumbous halides are not known, but it is reasonable to suppose that they are about the same as those of the mercuric halides (for bending, 3×10^{-12} ergs/radian²/molecule; for stretching, $2.5 \cdot 10^5$ dynes/cm./molecule; see Braune and Engelbrecht¹³).

If it be further assumed that the deviations from the mean bond length, l , or mean angle, θ , follow a Boltzmann distribution, values of $\overline{\delta l^2}$ and $\overline{\delta \theta^2}$ may be very easily calculated. At 600° K , the temperature at which stannous iodide was volatilised, $\sqrt{\overline{\delta l_{\text{Sn-I}}^2}} = 0.057 \text{ A}$, and $\sqrt{\overline{\delta \theta^2}} = 6.7^\circ$. Now $l_{\text{I-I}} = 2l_{\text{Sn-I}} \sin \theta/2$, and provided that $\delta l_{\text{Sn-I}}$ and $\delta \theta$ are as likely to be positive as they are negative, i.e. provided that the potential energy

¹³ Braune and Engelbrecht, *Z. physikal. Chem., B*, 1932, 19, 303.

functions of δl and $\delta \theta$ are symmetrical, as for simplicity we assume them to be, it can readily be shown that

$$\overline{\delta l_{I-I}^2} = 4 \sin^2 \theta/2 \overline{\delta l_{Sn-I}^2} + l_{Sn-I}^2 \cos^2 \theta/2 \overline{\delta \theta^2}. \quad (1)$$

Hence, in the above example, taking $\theta = 90^\circ$ and $l_{Sn-I} = 2.73$ A, we find $\sqrt{\overline{\delta l_{I-I}^2}} = 0.24$ A. The I—I term is thus clearly more sensitive to

TABLE VIII.

s	Part I. SnI ₂ . $\theta = 90^\circ$; $T = 600^\circ$ K.		Part II. SnI ₂ . $\theta = 180^\circ$; $T = 600^\circ$ K.		Part III. HgI ₂ . $\theta = 180^\circ$; $T = 400^\circ$ K.	
	Sn—I 0.057.	I—I 0.24.	Sn—I 0.057.	I—I 0.12.	Hg—I 0.047.	I—I 0.10.
0	1.000	1.000	1.000	1.000	1.000	1.000
2	0.993	0.891	0.993	0.972	0.996	0.980
4	0.974	0.631	0.974	0.891	0.983	0.923
6	0.943	0.355	0.943	0.772	0.963	0.835
8	0.900	0.158	0.900	0.631	0.932	0.726
10	0.848	0.056	0.848	0.487	0.895	0.606
12	0.789	0.016	0.789	0.355	0.853	0.487
14	0.725	0.0035	0.725	0.244	0.805	0.375
16	0.656	0.00063	0.656	0.158	0.754	0.278
Ratio	1.041		4.14		2.71	

temperature effects than is the Sn—I term, and when the corresponding coefficients for a series of s values are calculated as in Part I of Table VIII, it is seen that beyond $s = 6$ the theoretical curve is almost a pure $\sin sl/sl$

TABLE IX.—SnI₂.

$l_{Sn-I} = 2.73$ A.
I—Sn—I = 95° .

$s_{calc.}$ (corrected for thermal effect).	$s_{calc.}/s_{obsd.}$ (1.046)
2.98	4.07
5.12	6.28
7.48	8.63
9.77	10.91
12.08	
Mean	0.997
Average deviation	0.004
Thus final value of $l_{Sn-I} = 2.722$ A.	
Average deviation	0.011 A.

curve. When $s = 16$ the ratio of the coefficients is no less than 1.041 : 1, so the I—I term has become of negligible importance.

In Table IX the SnI distance is recalculated. The maxima and minima are those for a corrected theoretical curve with $l_{Sn-I} = 2.73$ A and I—Sn—I = 95° ; the ratios of $s_{calc.}/s_{obsd.}$ lead to a final value for $l_{Sn-I} = 2.72$ A with an average deviation of 0.011 A and a probable error of about 0.02 A, i.e. to one hardly different from that given by a simple 95° model. Since the discrepancy should be greatest for this compound the 95°

models are adequate for calculating bond-lengths in any other stannous halides or in the plumbous halides.

It can readily be shown that thermal vibration does not seriously affect the characteristic asymmetry of the maxima found in the simple

theoretical curves for linear models of the di-iodides, since the M—I and the I—I terms are affected to more nearly the same degree by temperature. According to equation (1), for these molecules with $\theta = 180^\circ$,

$$\overline{\delta l_{I-I}^2} = 4 \overline{\delta l_{M-I}^2}, \quad \text{whence } \sqrt{\overline{\delta l_{I-I}^2}}$$

for stannous iodide at 600°K , with $\theta = 180^\circ$, would be 0.114 \AA ; but since this relation is derived by differential methods, whereas the changes in l_{Sn-I} and especially in θ are not infinitesimal, this value is not precise. If the effect of the former change be neglected it can be shown that the

second alone would make $\sqrt{\overline{\delta l_{I-I}^2}} = 0.01 \text{ \AA}$. A more exact treatment would not be warranted, in view of the other approximations made, and

so calculations have been made for $\sqrt{\overline{\delta l_{I-I}^2}} = 0.12 \text{ \AA}$ in stannous iodide, and corresponding with 0.10 \AA (at 400°K) for mercuric iodide⁵; the results are given in Parts II and III of Table VIII. The importance of the I—I term is not seriously reduced for s values below about 14, and none of the rings for dihalides which we have observed fall beyond this point, owing to limitations imposed by the apparatus. Furthermore, although the absolute values of the coefficients at $s = 16$ are distinctly less than unity, the sixth maximum on the total intensity curve is then reached and, for a $\sin s/l$ curve, this has an intensity only one-fifth that of the first, so the extra decrease caused by the temperature effect, up to that point, is of little importance. Thus, for the range $s = 0$ to $s = 14$, with which our present work is concerned, temperature has little effect upon the theoretical curves for linear models of the dihalides, but it has a very marked effect upon those for right-angled models.

Maxima with the characteristic saw-tooth asymmetry were observed with mercuric iodide⁵ but they were not for stannous iodide. We therefore conclude that although in the former the valency angle is probably 180° , in the latter it is certainly considerably less, although we cannot say within narrow limits what it is.

Cadmium chloride, bromide, and iodide.

The photographs from these substances all showed regularly spaced rings, which diminished steadily in intensity from the centre outwards. All the rings were unsymmetrical, rising more steeply on the inside, and the minima were correspondingly steeper on the outside. This asymmetry was least marked in the chloride, and most in the iodide, where the rings had the appearance of thin, intense maxima with weak shelves outside them. In the iodide this asymmetry was quite marked in the sixth ring, though the seventh was so weak as not to show it very clearly.

These all agree with the theoretical curves for models with cadmium valency angles of 180° (Fig. 3). No other model produces the

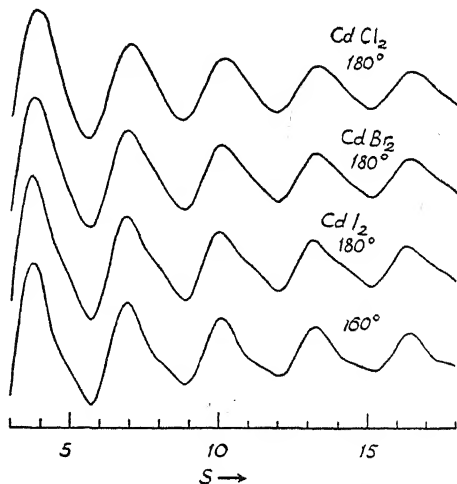


FIG. 3.—Theoretical intensity curves for cadmium halides.

TABLE X.—CdCl₂.

Max.	Number of Photographs.	S _{obsd.}	Scale, for Cd—Cl = 2 Å.	l _{Cd—Cl} .	Mfn.	Number of Photographs.	S _{obsd.}	Scale, for Cd—Cl = 2 Å.	l _{Cd—Cl} .
1	6	3.56	3.78	(2.13)	2	6	5.03	5.54	2.205
2	6	6.27	6.96	2.220	3	6	7.83	8.68	2.233
3	6	9.01	10.10	2.243	4	6	10.52	11.12	2.248
4	6	11.72	13.26	2.261					
Mean	.	.	.	2.241					2.229
Average deviation	.	.	.	0.014					0.016

Mean Cd—Cl length from maxima = 2.241

Mean Cd—Cl length from minima = 2.229

Total mean: Cd—Cl = 2.235 Å.

characteristic saw-tooth asymmetry of the maxima and the consequent nearness of each minimum to the subsequent maximum.

Assuming an angle of 180°, a value of the cadmium-halogen distance can be calculated from each maximum and minimum. However, owing to the St. John effect¹² all the maxima will be observed too far in and all the minima too far out. Hence all bond lengths calculated from the maxima will be too large and from the minima too small. The final value chosen for the bond length of each halide was therefore the mean of the means of the values from the maxima, and of the values from the minima.

The results for cadmium chloride are given in Table X. The theoretical *s* values, calculated from a model with an arbitrary Cd—Cl distance of 2 Å, are given in the 4th and 9th columns. The results for cadmium bromide are given in Table XI, and for cadmium iodide in Table XII.

The radial distribution curve calculated from estimated intensities of maxima alone (Fig. 2) gives peaks at 2.61 and 5.02 Å (heavy arrows) which, while still agreeing quite well with the SnI length derived above from maxima alone, indicates an I—Sn—I angle of about 160°. In order further to explore the possibility that the I—Cd—I angle is not

TABLE XI.—CdBr₂.

Max.	Number of Photographs.	Sobsd.	Scale. for Cd—Br = 2 A.	I _{Cd—Br} .	Min.	Number of Photographs.	Sobsd.	Scale. for Cd—Br = 2 A.	I _{Cd—Br} .
1	8	3.24	3.72	(2.30)	2	9	4.86	5.62	(2.31)
2	10	5.79	6.89	2.377	3	10	7.43	8.77	2.355
3	10	8.40	10.04	2.392	4	10	10.10	11.91	2.356
4	10	11.01	13.19	2.397	5	7	12.58	15.05	2.393
5	7	13.48	16.34	2.423	6	3	15.24	18.20	2.386
6	6	16.06	19.48	2.426	7	—	—	—	—
7	3	18.61	22.62	2.431					
Mean	.	.	.	2.407					2.372
Average deviation	.	.	.	0.019					0.017

Mean Cd—Br length from maxima = 2.407

Mean Cd—Br length from minima = 2.372

Total mean : $\text{Cd—Br} = 2.390 \text{ A.}$

TABLE XII.—CdI₂.

Max.	Number of Photographs.	Solsd.	Scale. for Cd—I = 2 Å.	I _{Cd—I} .	Min.	Number of Photographs.	Solsd.	Scale. for Cd—I = 2 Å.	I _{Cd—I} .
1	12	3.02	3.68	(2.44)	2	12	4.56	5.67	(2.49)
2	12	5.35	6.85	2.559	3	12	6.96	8.81	2.531
3	12	7.83	9.99	2.552	4	12	9.41	11.96	2.542
4	12	10.23	13.14	2.570	5	12	11.79	15.10	2.563
5	12	12.64	16.29	2.577	6	4	14.25	18.26	2.563
6	6	15.00	19.43	2.590	7	—	—	—	—
7	5	17.44	22.57	2.580					
Mean	.	.	.	2.573					2.550
Average deviation	.	.	.	0.012					0.013

Mean Cd—I length from maxima = 2.573

Mean Cd—I length from minima = 2.550

Total mean : $\frac{\text{Cd—I} = 2.562 \text{ Å.}}{\text{Cd—I} = 2.562 \text{ Å.}}$

180°, but rather less, a curve (Fig. 3) was calculated for an angle of 160°. It shows that even at the fourth maximum the rings have lost much of their characteristic "saw tooth" appearance, which is visible even in the sixth ring on the plates. Further, a model of 160° would give less consistent Cd—I distances. The angle in cadmium iodide may be taken as > 160°, probably 180°, and the same applies with less certainty to the bromide and chloride. The results for the cadmium halides are summarised in Table opposite.

Halogen.	$l_{\text{Cd-X}}$ in Å.	Angle.
Cl .	$2.23(5) \pm 0.03$	$180^\circ \pm 10^\circ$
Br .	2.39 ± 0.03	$180^\circ \pm 10^\circ$
I .	2.56 ± 0.03	$180^\circ \pm 10^\circ$

(See also Hassel and Strömme,¹⁴ who report $l_{\text{Cd-I}} = 2.596 \pm 0.02$ Å in cadmium iodide from four maxima, in good agreement with the result here given from maxima alone.)

Discussion.

The bond lengths found in the zinc and cadmium halides are less than the respective sums of the normal covalent radii assigned by Pauling and Huggins,¹⁵ by 9.5, 8.8 and 8.9 % for chloride, bromide, and iodide respectively, and a possible explanation of this fact is that they have some degree of double-bond character (*cf.* mercuric halides^{3, 5}).

No radii have been assigned to stannous tin or to plumbous lead, so no normal, single-bond lengths can be calculated for comparison with the observed ones; and consequently there is no obvious, direct means of deciding whether or not these bonds are abnormal. It is to

TABLE XIII.

		Cl.	Br.	I.
Sn ^{II}	l_{SnX}	2.42 ± 0.03	2.55 ± 0.02	2.73 ± 0.02
	Halogen radius	0.99	1.14	1.33
	Sn ^{II} radius	1.43	1.41	1.40
Pb ^{II}	l_{PbX}	2.46 ± 0.02	2.60 ± 0.03	2.79 ± 0.02
	Pb ^{II} radius	1.47	1.46	1.46
Tl ^I	l_{TlX}	2.55^\dagger	2.68^\dagger	2.87^\dagger
	Tl ^I radius	1.56	1.54	1.54

† Grether.¹⁶

compound to compound. It is true that the radii so calculated from the be noticed, however, that if values of the apparent radii for the metals in these states be calculated from the several halide bond lengths, by subtracting the normal halogen radii, they are found to be sensibly constant in the series for each element, as are the values for thallous thallium derived from the thallous halides. This fact suggests that these apparent radii are the actual covalent radii, for it would be expected that when contraction occurs the apparent radii would vary from contracted halides of certain elements vary very little; but it is then

¹⁴ Hassel and Strömme, *Z. physikal. Chem.*, B, 1938, 38, 466.

¹⁵ Pauling and Huggins, *Z. Krist.*, A, 1934, 87, 205.

¹⁶ Grether, *Ann. Physik*, 1936, 20, 1.

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found, as the examples in Table XIV show, that similar values for the element immediately above or below in their Groups show considerable variation.

TABLE XIV.

	Cl.	Br.	I.	Range.
Cd ^{II} radius .	1·245	1·25	1·23	0·015
Hg ^{II} radius .	1·35§	1·30§	1·28§	0·07
Ge ^{IV} radius .	1·09*	1·15*	1·17*	0·08
Sn ^{IV} radius .	1·31*	1·30*	1·31*	0·01
As ^{III} radius .	1·17§	1·22§	1·25§	0·08
Sb ^{III} radius .	1·38§	1·38§	1·42§	0·04

§ Gregg *et al.*⁵ These values are preferred to those given by Braune and Knoke.³

* Lister and Sutton.¹⁷

Both the stannous and the plumbous series, however, give constant series of values.

A more positive indication that the bonds in the stannous and plumbous halides are not shortened is that the divalent radii calculated above are as great as the normal values for the tetravalent radii, being 1·41 and 1·46 Å as compared with 1·40 and 1·46 respectively; yet, so far as is known, atoms have larger radii in their higher valency states than in their lower ones (*cf.* boron,¹⁸ phosphorus¹⁹).

If the contractions observed in the cadmium and mercuric halides are correctly explained by the theory that they have some double-bond character, it is surprising that the bonds in the stannous, plumbous, and thallos compounds are normal; for the tin, lead, and thallium atoms have incomplete octets, and might therefore be expected to accept co-ordinate links from the halogen atoms, just as cadmium and mercury are supposed to do, especially since one such bond could be formed without splitting the *s* pairing, if the third *p* orbital were used (*see later*). This expectation is supported by the fact that both stannous and plumbous halides readily form complexes of the type $[MCl_3]^-$ just as the cadmium and mercuric halides do.

A further conclusion to be drawn from the constancy of the apparent radii is that the bonding orbitals used by the metal atoms are the same in all the halides. This is consistent with the view that the stannous and plumbous states exist stably because it is comparatively difficult to break the pairing of the *s* electrons in the valency group; for then it would be expected that the two bonds formed would utilise pure *p* orbitals (5*p* and 6*p* for tin and lead respectively). Should this surmise be correct, the predicted valency angle would be about 90°. As was explained in the experimental section, it is impossible to determine the valency angle in these compounds with any precision, but we can at least be certain that it is considerably less than 180°, and is therefore quite different from that found in the zinc, cadmium, and mercury compounds, as our view requires.

¹⁷ Lister and Sutton, *preceding paper*.

¹⁸ Lévy and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 2085.

¹⁹ Brockway and Beach, *ibid.*, 1938, **60**, 1836.

There is an interesting difference between the length which we find for the Pb—Br link in the free, gas-phase molecule, and that found by Powell and Tasker⁶ in the molecule when it is incorporated into the complex crystal lattices of the double salts ammonium, potassium, or rubidium pentabromo-diplumbite. In these latter it is 2.89 ± 0.05 Å, which is no less than 0.29 Å greater than the distance which we observed and, as these authors pointed out, is intermediate between the values to be anticipated for a covalent and for a purely ionic bond.

Summary.

The structures of the chlorides, bromides and iodides of cadmium, and of divalent tin and lead have been examined by the electron diffraction method. It has been shown that the cadmium halides are probably linear molecules while the others certainly are not.

The bond lengths found were

$$\begin{array}{ll} l_{\text{Cd-Cl}} = 2.23(5) \pm 0.03 \text{ Å}, & l_{\text{Cd-Br}} = 2.39 \pm 0.03 \text{ Å}, \\ & l_{\text{Cd-I}} = 2.56 \pm 0.03 \text{ Å}; \\ l_{\text{Sn-Cl}} = 2.42 \pm 0.02 \text{ Å}, & l_{\text{Sn-Br}} = 2.55 \pm 0.02 \text{ Å}, \\ & l_{\text{Sn-I}} = 2.73 \pm 0.02 \text{ Å}; \\ l_{\text{Pb-Cl}} = 2.46(5) \pm 0.02 \text{ Å}, & l_{\text{Pb-Br}} = 2.60 \pm 0.03 \text{ Å}, \\ & l_{\text{Pb-I}} = 2.79 \pm 0.02 \text{ Å}. \end{array}$$

The cadmium-halogen bond lengths are less than the sums of the appropriate Pauling-Huggins covalent radii, but those of the tin-halogen or lead-halogen bonds are close to the sums of the tetrahedral covalent radius for tin or lead and the appropriate halogen radius. The latter fact is interpreted as meaning that the covalencies in stannous and plumbous compounds involve only *p*-orbitals on the metal atom.

The authors wish to thank Mr. D. Ll. Hammick and Professor N. V. Sidgwick for their interest and advice, The Royal Society and Imperial Chemical Industries Ltd. for loan of apparatus, and the Department of Scientific and Industrial Research for a maintenance grant to one of them (M. W. L.).

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A THERMODYNAMIC STUDY OF BIVALENT METAL HALIDES IN AQUEOUS SOLUTION. PART VIII. THE ACTIVITY COEFFICIENT OF FERROUS CHLORIDE.

BY R. H. STOKES AND R. A. ROBINSON.

Received 5th June, 1941.

Isopiestic measurements have been made of the activity coefficients of the chlorides of five elements in the first transitional group,¹ viz. Mn, Co, Ni, Cu, Zn. The first three of these chlorides have activity coefficients resembling those of the alkaline earth chlorides, indicating that they belong to the class of strong electrolytes. A reasonably accurate

¹ Robinson and Stokes, *Trans. Faraday Soc.*, 1940, 36, 740, 1137.

prediction of the activity coefficient of FeCl_2 can be made by assuming that the values will lie between those of MnCl_2 and CoCl_2 at comparable concentrations. It is nevertheless desirable to have experimental confirmation to guard against the possibility of anomalous behaviour.

We have now been able to modify the isopiestic technique for use with salts, such as FeCl_2 , which are liable to atmospheric oxidation. With this modified technique the solution may be prepared in an inert atmosphere, introduced into the silver dishes, and brought into equilibrium with the reference solution without contact with the air.

Experimental.

The apparatus used is shown in the figure. The body of the desiccator, the Cu block and the Ag dishes are of the form used in other isopiestic

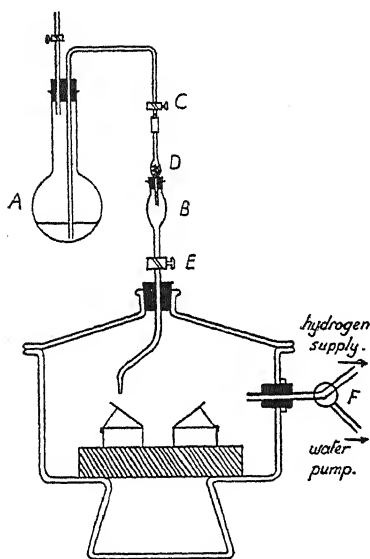


FIG. 1.—Apparatus for using isopiestic method in an inert atmosphere.

measurements. The lid of the desiccator carries a small dropping funnel B, fitted into a soft rubber stopper which forms a flexible joint. The flask of solution A is connected to the funnel through a small bulb D, packed with glass wool, which serves to remove particles of iron from the solution in a later operation. A stock solution of FeCl_2 is prepared in the flask by the action of pure HCl on an excess of "reduced" Fe, the apparatus being disconnected below the stopcock C in order that a current of H_2 may be passed through the flask. Two of the four Ag dishes are weighed empty and placed on the Cu block, the others containing weighed amounts of KCl solution. The flask is connected at C and, with tap E open and tap C closed, the apparatus is repeatedly evacuated and filled with H_2 by means of the two-way stopcock F, the last admission of H_2 being stopped at about half atmospheric pressure. The tap E is closed and C opened to admit a few c.c. of solution through the glass wool filter

into B. The funnel is then manipulated in its flexible joint so that the solution can be run through the stopcock and capillary tube E, into each of the empty dishes. The tap E is then closed and the desiccator evacuated and rocked in the thermostat until equilibrium is established. The desiccator is then opened, free access of air having a negligible effect at this stage, and the dishes are weighed. The two FeCl_2 solutions are then analysed gravimetrically for chloride so that the equilibrium concentrations of both salts are known. The duplicate solutions were found to agree within 0.1 %.

The results obtained are given in Table I. No measurements were made below 0.3 M. because the amount of chloride is then too small for accurate gravimetric analysis. The data obtained above 0.3 M. were sufficient to establish that the activity coefficient of this salt is intermediate between those of MnCl_2 and CoCl_2 . The method could be extended, if desired, to solutions between 0.1 and 0.3 M. by using electrometric methods of chloride analysis.

TABLE I.—ISOPIESTIC SOLUTIONS OF POTASSIUM CHLORIDE AND FERROUS CHLORIDE.*

KCl.	FeCl ₂ .	KCl.	FeCl ₂ .	KCl.	FeCl ₂ .	KCl.	FeCl ₂ .
0.4565 1.871 4.374	0.3132 1.056 2.050	0.5355 2.442	0.3625 1.309	0.912 3.340	0.576 1.664	1.300 3.467	0.7876 1.723

* The numerical data refer to molalities of isopiestic solutions.

The activity coefficients calculated from these isopiestic results are given in Table II.

TABLE II.—ACTIVITY COEFFICIENTS OF FERROUS CHLORIDE AT 25°.

<i>m.</i>	<i>γ.</i>	<i>m.</i>	<i>γ.</i>	<i>m.</i>	<i>γ.</i>	<i>m.</i>	<i>γ.</i>
0.1	0.525	0.5	0.460	0.9	0.501	1.6	0.668
0.2	0.480	0.6	0.467	1.0	0.519	1.8	0.739
0.3	0.463	0.7	0.475	1.2	0.558	2.0	0.817
0.4	0.459	0.8	0.486	1.4	0.607	—	—

Summary.

A modification of the isopiestic vapour pressure method is described in which access of atmospheric oxygen is avoided. The method is used to determine the activity coefficient of ferrous chloride. In respect to its activity coefficient ferrous chloride occupies a regular position in the series : manganese, iron, cobalt and nickel chloride.

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THE SECOND VIRIAL COEFFICIENT OF ACETALDEHYDE.

BY E. A. ALEXANDER AND J. D. LAMBERT.

Received 17th June, 1941.

The purpose of this paper is to describe an investigation of the second virial coefficient of acetaldehyde. This was originally undertaken in order to obtain an equation of state for application to acoustic measurements and revealed interesting anomalies which may be interpreted in terms of a partial polymerisation of acetaldehyde vapour.

Experimental.

Acetaldehyde was carefully fractionated, using a tall fractionating column. The middle fraction was distilled into the storage bulb of the apparatus under reduced pressure, during which process the first and last

fractions were again discarded. The acetaldehyde was now protected from light and used as required.

Measurements were taken with the all-glass apparatus shown in Fig. 1, which is in principle an ordinary Boyle's law apparatus. The tubes (A) and (B) have an internal diameter of one centimetre, and (A) is graduated in tenths of a cubic centimetre. They are kept at constant temperature by a water jacket (C) through which a fast stream of water from a large thermostat is circulated. Alterations in the mercury levels are controlled by the mercury valve (D). The pressure inside the mercury reservoir (E) is increased or decreased via a three-way tap (F), which is coupled to a vacuum pump and to a nitrogen cylinder. The range of the apparatus can be increased by evacuating the limb (B). The mercury levels and the volume of the gas in the limb (A) are read with an accurate cathetometer. The mercury menisci are screened and illuminated from behind. The apparatus is calibrated and tested with pure air and carbon dioxide respectively.

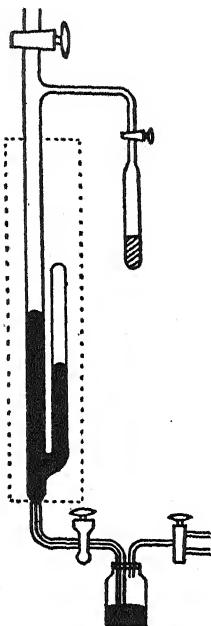


FIG. 1.

Results.

The second virial coefficient is obtained from the equation of state,

$$PV = n(RT + BP),$$

where P is the pressure, V the volume, n the number of mols, T the absolute temperature, and B the second virial coefficient.

The plots of PV against P for samples of acetaldehyde at different temperatures give good straight lines, from which the value of B is deduced. The plot at 40.0°C. is shown in Fig. 2. The values of

B at temperatures between 15.0°C. and 99.9°C. are shown in Fig. 3, curve 1.

Some measurements with glass wool packed in the top of the limb (A), Fig. 1, were made, and these are also shown in Fig. 3, curve 1.

Rough measurements at higher temperatures were taken with the modified constant pressure apparatus of Schäfer.¹ The values of B at temperatures between 60°C. and 300°C. are also shown in Fig. 3, curve 1.

Comparison with the Theoretical Value of B .

The value of B may also be calculated from critical data by the Berthelot equation,

$$B = (9RT_c/128P_c)/(1 - 6T_c^2/T^2),$$

where T_c and P_c are the critical temperature and pressure respectively. The critical values for acetaldehyde are 188°C. and 63.2 atmospheres,² hence

$$B = 42.1 - 53.6 \times 10^6/T^2 \text{ c.c./mol.}$$

The plot of B calculated from the above equation, against T is shown in Fig. 3, curve 2.

A large discrepancy exists at ordinary temperatures. The Berthelot equation is known to give excellent agreement with experimental results for a wide range of compounds. Consequently it was desirable to check

¹ Schäfer, *Z. physik. Chem.*, B, 1937, 36, 85.

² Landolt-Börnstein's Tables.

the two methods of obtaining B with another substance. A spectroscopically pure sample of diethyl ether was chosen for this purpose.

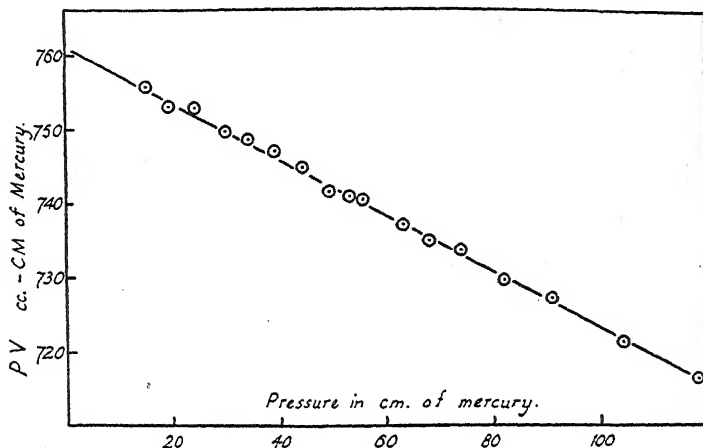


FIG. 2.

The value of B at 40.0°C . obtained with the Boyle's law apparatus is -1128 c.c./mol. The critical values are 193.8°C . and 35 atmospheres,² hence, from the Berthelot equation at 40.0°C ., B is -1141 c.c./mol. The agreement between the two methods is thus within 1 % for diethyl ether, whereas for the acetaldehyde under the same conditions, B is -959 c.c./mol. and -506 c.c./mol. respectively. Hence, it is apparent that this discrepancy is due to some specific property of the acetaldehyde.

Discussion.

The discrepancy between the calculated and observed values of B may be due either to adsorption or polymerisation. Adsorption, however, does not seem to explain this, as there is practically no difference in the value of B , when the surface-volume ratio is increased by the addition of glass wool.

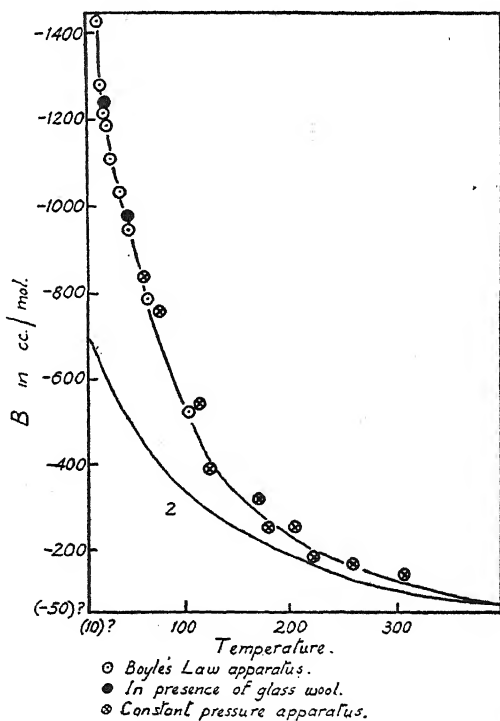
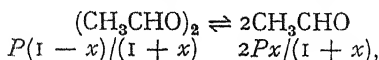


FIG. 3.

If a reversible polymerisation is assumed, of the type



where $(1-x)$ is the degree of polymerisation and P the total pressure, then the equilibrium constant will be given by:—

$$K_p = 4Px^2/(1-x^2).$$

The degree of polymerisation may be calculated from the experimental results if it is assumed that the true second virial coefficient of monomeric acetaldehyde vapour is given by the Berthelot equation, that is, that the degree of polymerisation at the critical temperature is negligible. The calculation of x is illustrated with the aid of Fig. 4. B_o and B_c are the observed and calculated values of the second virial coefficient

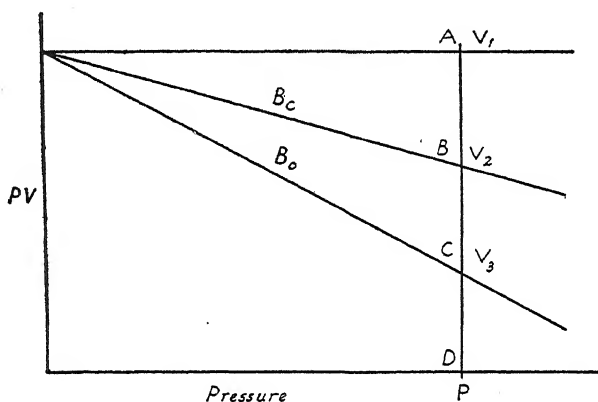


FIG. 4.

respectively, and are proportional to the slopes of curves 3 and 2 respectively. Hence, geometrically at a particular pressure P ,

$$\frac{B_c}{B_o} = \frac{AD - BD}{AD - CD}$$

$$= \frac{PV_1 - PV_2}{PV_1 - (P_a + P_d)V_3},$$

where P_a and P_d are the partial pressures of monomeric and polymerised acetaldehyde vapour respectively.

$$\begin{aligned} \text{And for curve (1) } PV_1 &= nRT \\ \text{,, ,, ,, (2) } PV_2 &= n(RT + B_cP), \\ \text{,, ,, ,, (3) } PV_3 &= n(RT + B_oP). \end{aligned}$$

Therefore,

$$\frac{B_c}{B_o} = \frac{nRT - n(RT + B_cP)}{nRT - \{n_a(RT + B_aP_a) + n_d(RT + B_dP_d)\}}$$

where n_a and n_d are the number of mols of monomeric and polymerised acetaldehyde respectively, and B_d is the second virial coefficient of the polymer. From the above equilibrium n , n_a and n_d are proportional to 2 , $2x$ and $(1-x)$ respectively, and if the degree of polymerisation is

small P_a is approximately equal to P and $B_d P_d$ is negligible, then it follows that

$$x = \frac{RT + P(2B_0 - B_c)}{RT + PB_c}.$$

The calculation of K_p for acetaldehyde at 40.0° C. at different pressures is given below :—

Press. (atmos.)	0.1	0.25	0.5	0.75	1.0	1.25	1.5
x	0.9975	0.9908	0.9883	0.9718	0.9640	0.9539	0.9451
K_p (atmos.)	50.9	53.3	54.6	51.0	51.6	50.3	49.2

The average value is 51.6. The constancy of K_p (within the limits of experimental error) at different pressures is significant as evidence in favour of the polymerisation. K_p is calculated at different temperatures for the most accurate results (the Boyle's law apparatus between 15.0° C. and 40.0° C.), and the plot of $\log_{10} K_p$ against $1/T$ is shown in Fig. 5. This

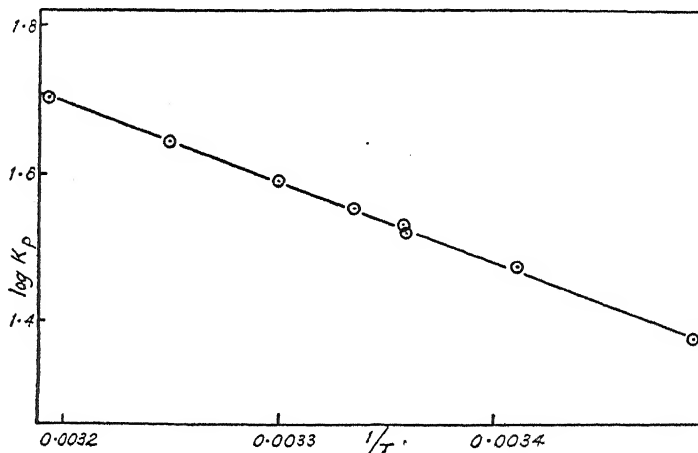


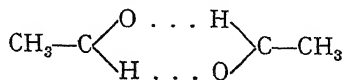
FIG. 5.

gives a straight line of slope corresponding to

$$K_p = 2.29 \times 10^5 \times e^{-5226/RT}, \text{atmos.},$$

thus the heat of polymerisation is 5.226 Kcal./mol.

If it is assumed that the polymer has the structure



by analogy with formic and acetic acids, then the value of 2.6 Kcal./mol. may be assigned to the strength of the C—H . . . O hydrogen bond. This is compared with some typical hydrogen bonds below :—

Bond	C—H . . . N	C—H . . . O	N—H . . . N
Energy ³ (Kcal./mol.)	3.3	2.6	1.3

³ Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, 1939).

Hence the value assigned to the C—H . . . O hydrogen bond does not seem unreasonable.

Summary.

The second virial coefficient of acetaldehyde was measured and calculated from the Berthelot equation. There is a large discrepancy between the two values which may be accounted for in terms of a polymerisation with a heat of 5.226 Kcal./mol.

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ON THE STRUCTURE OF CONDENSED MONOMOLECULAR FILMS.

BY A. E. ALEXANDER.

Received 12th June, 1941.

1. Discussion of Earlier Theories.

The most general type of force-area (F — A) curve of a completely condensed monolayer is that given in Fig. 1, consisting of two approximately linear sections, the first (XY) showing a much higher compressibility than the second (YZ). Deviations from linearity only appear to exist along XY , and then generally only at the low pressure end of the curve. In some cases (e.g. stearic or palmitic acids at neutral pH,¹ calcium stearate²), XY is missing and only YZ appears; in others (e.g. the nitriles³) the reverse is the case. A survey of the literature shows that the areas at Y' (obtained by extrapolating YZ to $F = 0$) lie between 19 and 21 Å² for all the straight-chain compounds studied, whereas those obtained by similarly extrapolating XY (giving the area X') show a much wider variation, lying in general between 22 and 30 Å².

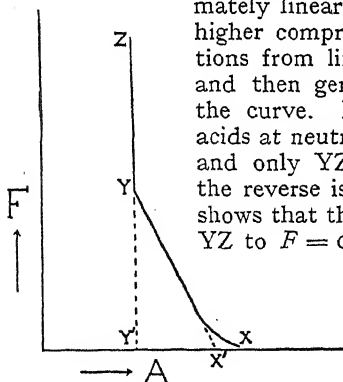


FIG. 1.

Condensed films were early differentiated as fluid or solid by means of the motion of dust or talc particles on the surface when blown by a small air jet. Recently this method has been made more quantitative by determination of the surface viscosity, either by means of the flow through a slit, or by the damping of suitable systems when oscillating in the surface.⁴ Sensitive tests for rigidity can be obtained by the oscillating vane, talc mobilities and the behaviour of floating strips of

¹ Adam, *Proc. Roy. Soc., A*, 1921, 99, 336.

² Harkins and Anderson, *J.A.C.S.*, 1937, 59, 2189.

³ (a) Adam, *Proc. Roy. Soc., A*, 1922, 101, 452; (b) Adam and Harding, *ibid.*, 1933, 143, 104.

⁴ (a) Joly and Dervichian, *Nature*, 1938, 141, 975; *J. Chem. Physics*, 1938, 6, 226; (b) Harkins and others, *J. Physical Chem.*, 1938, 42, 897; *J.A.C.S.*, 1940, 62, 3155.

paper,⁵ or alternatively by the method of Mouquin and Rideal.⁶ Such measurements readily show up any phase changes in the film, and allow differentiation between true fluid films (Newtonian flow), anomalous fluid or plastic solid films (non-Newtonian flow), and true solid films (showing a definite elastic modulus and yield-point). The results of such measurements are not discussed in detail here, but in a general way it can be stated that simple derivatives of long-chain compounds tend to give fluid films along XY, whereas along YZ fluid, plastic solid and true solid states are observed.

Many attempts to draw analogies between two-dimensional films, particularly the condensed, and three-dimensional matter, have been put forward. The most obvious suggestion, that the two regions XY and YZ corresponded to the fluid and solid states respectively, cannot be correct, since certain compounds, *e.g.* alcohols and esters, give fluid films in both. Adam¹ suggested that the two parts XY and YZ could be ascribed to the close-packed heads and close-packed chains respectively. Lyons and Rideal⁷ suggested that the chains were inclined at either 26.5° or 45° to the vertical, since tilting at such angles allowed the zig-zag chains to interlock. Taking the cross-section of the chain as 18.5 \AA^2 ,⁸ this would give 20.7 and 26.2 \AA^2 for the Y' and X' areas respectively. This was criticised by Adam,⁹ who pointed out that although there was some evidence for the first interlocking position, there was none at all for the second. Adam's most recent view is:¹⁰ "Though it is practically certain that the long-chains are closely packed when curve I (YZ in Fig. 1) is obtained, it is not, however, certain that they are vertical." With regard to the XY portions, he concludes (p. 53¹⁰) that these give a measure of the cross-section of the head-groups as packed in films, and that these may be subdivided into two groups, according as to whether they are, or are not, rearranged by compression. Those with a high compressibility, *e.g.* fatty acids on acid solution, nitriles and acetamides, fall into the first class; those with much lower compressibilities, *e.g.* phenols, resorcinols, ureas and monoglycerides, into the second. The idea of head-group compression along XY was criticised by Schulman and Hughes¹¹ from their surface potential measurements on the alcohols, since they found that μ (the vertical component of the apparent dipole moment) remained sensibly constant in this region, and they suggested as an alternative the expulsion into the substrate of solvent molecules oriented between the polar groups.

A recent paper by Dervichian¹² seeks to draw analogies between monolayers and three-dimensional matter in very much greater detail. Gaseous, expanded and condensed films are discussed, but only his interpretation of the latter will be considered here. The particularly close analogy which he draws between condensed films and the three-dimensional state is shown by the following statement (p. 939¹²): "The lattice structure and the tilt of the molecules in the different forms are the same in two and three dimensions." Harkins and Boyd¹³ have

⁵ Langmuir and Schaefer, *J.A.C.S.*, 1937, **59**, 2400.

⁶ Mouquin and Rideal, *Proc. Roy. Soc. A*, 1927, **114**, 690.

⁷ Lyons and Rideal, *ibid.*, 1929, **124**, 322.

⁸ (a) Müller, *ibid.*, 1927, **114**, 542; 1928, **120**, 437; (b) *Ibid.*, 1930, **138**, 514.

⁹ Adam, *ibid.*, 1930., **126**, 526.

¹⁰ Adam, *The Physics and Chemistry of Surfaces*, 2nd edit. O.U. Press, 1938.

¹¹ Schulman and Hughes, *Proc. Roy. Soc. A*, 1932, **138**, 430.

¹² Dervichian, *J. Chem. Physics*, 1939, **7**, 931.

¹³ Harkins and Boyd, *J. Physical Chem.*, 1941, **45**, 20.

criticised this theory on the grounds that firstly, the accurate measurements of Nutting and Harkins¹⁴ upon the acids do not agree at all well with his theoretical values and, secondly, that the liquid condensed phase (XY in Fig. 1) cannot be crystalline (as postulated by Dervichian), since their viscosity measurements in this region exactly fit the theory of *liquid* monolayers developed by Moore and Eyring.¹⁵

In addition, there would seem to be many other points which are in contradiction to Dervichian's simple theory, and they are briefly enumerated below.

(1) Considering compounds where the polar groups are associated in the crystal and the molecules are inclined (*e.g.* fatty acids, alcohols), it seems very improbable on general grounds that the replacement of one polar group by water molecules would be without influence on the molecular packing, since in compounds which are non-polar (*e.g.* hydrocarbons),⁸ or have non-associated polar groups (*e.g.* ketones other than the methyl),¹⁶ the normal packing is the vertical one.

(2) A monolayer structure strictly identical with that in the crystal should mean that any compound solid at room temperature should give solid condensed monolayers at that temperature. Very many examples indeed are known where this is untrue. Thus many unsaturated acids and alcohols,¹⁷ many α -substituted acids (even as the calcium salts), *e.g.* α -methyl palmitic, α -triazole palmitic, α -bromo-stearic¹⁸; lauric and myristic acids at pH 2, heptadecyl methyl ketone,¹⁹ many esters,²⁰ saturated alcohols,¹¹ and so on, all give freely fluid monolayers at room temperature. In fact, it would seem that in *no definite* case is the melting-point of the monolayer as high as that in the crystal. The one example quoted by Dervichian, namely cetyl alcohol (M.P. in film quoted as ca 50°, M.P. crystal 49.5°) does not appear to be correct, since, as recently shown by Fourt and Harkins²¹ and Trapeznikov,²² this compound gives true fluid films below the kink point Y and anisotropic fluid films above that point. Dervichian overcomes this objection by postulating the existence of vitreous forms stable in monolayers but unknown in three dimensions (p. 947¹²). Based upon the one example given (the triglycerides) this appears much too speculative.

(3) In several well-established cases the monolayer structure *must* be different from that in the crystal. Cetyl palmitate,²⁰ pentaerythritol tetrapalmitate,²³ and tripalmitin^{24, 25} are examples showing approximately parallel long-chain orientation in the monolayer (as shown by the area per molecule occupied) and opposed long-chain orientation in the crystal. Also with the glycerides and esters generally it is known that in the crystal only the *trans* form can exist, whereas both *cis* and *trans* can, and do, exist in the condensed monolayers.²⁵

(4) A comparison between the height of the monolayer on the water surface as determined optically, and the long X-ray spacing of the

¹⁴ Nutting and Harkins, *J.A.C.S.*, 1939, **61**, 1180.

¹⁵ Moore and Eyring, *J. Chem. Physics*, 1938, **6**, 391.

¹⁶ Oldham and Ubbelohde, *Trans. Faraday Soc.*, 1939, **35**, 328.

¹⁷ Marsden and Rideal, *J. Chem. Soc.*, 1938, 1163.

¹⁸ Alexander, *ibid.*, 1939, 777.

¹⁹ Hoffman, Ralston and Ziegler, *J. Physical Chem.*, 1939, **43**, 301.

²⁰ Alexander and Schulman, *Proc. Roy. Soc., A*, 1937, **161**, 115.

²¹ Fourt and Harkins, *J. Physical Chem.*, 1938, **42**, 897.

²² Trapeznikov, *Acta Physicochim. U.R.S.S.*, 1938, **9**, 273; 1939, **10**, 65.

²³ Adam and Dyer, *Proc. Roy. Soc., A*, 1924, **106**, 694.

²⁴ Clarkson and Malkin, *J. Chem. Soc.*, 1934, 666.

²⁵ Alexander, *ibid.*, 1939, 177.

crystal (both determined from the same built-up film),^{18, 26, 27} shows that there is no fixed relationship between the two. With one exception (α -triazo-palmitic acid), the same X-ray spacing is obtained regardless of the deposition pressure. On Dervichian's theory the optical and X-ray spacings should be intimately related, and different crystalline forms might well have been expected when depositing at different molecular areas.

(5) Recent work by Trapeznikov,²² and by Nutting and Harkins,¹⁴ on the surface areas and viscosities of alcohols, acids and esters, show no sign of singular points other than those previously well established by numerous earlier workers, as shown in Fig. 1. With regard to the surface viscosity measurements, however, the oscillating methods do not appear to be as sensitive as the slit method used by Dervichian and Joly.

(6) On Dervichian's hypothesis the characteristic areas in condensed films should be independent of the chain-length, since the tilt of the molecules in a given crystal form is well-known to remain independent of this. Recent very accurate measurements by Nutting and Harkins¹⁴ indicate a slight, but significant, decrease with increasing chain length both in the acids and alcohols. This had previously been noted by Adam and Dyer²³ and by Schulman and Hughes.¹¹

(7) According to Dervichian, collapse of condensed films always occurs at an area of about 18.5 \AA^2 for straight-chain compounds, *i.e.* at the minimum cross-sectional area occupied by the chain in the crystal. Actually an examination of the literature shows that collapse seems to occur *invariably* at greater areas than found in the crystal. In no case, so far as can be seen, is an area below 19 \AA^2 obtained with *stable* films, as compared with the usual values of about 18.3 \AA^2 for the crystal (*e.g.* stearic acid). Nutting and Harkins¹⁴ give no area less than 19 \AA^2 (estimated error 0.16 %), and that is for the C_{20} acid; the usual area at the kink-point Y being 19.20 \AA^2 .

With the methyl ketones the minimum area given by Adam, Danielli and Harding²⁸ is 19.5 \AA^2 at 21 dynes ($T = 17^\circ$), and 19.6 \AA^2 at 44 dynes ($T = 25^\circ$) by Hoffman, Ralston and Ziegler.¹⁹ The recent accurate X-ray measurements on these ketones give a cross-sectional area of 18.23 \AA^2 (vertical molecules).¹⁶ There are other examples, but these seem to be some of the most accurate measurements.

(8) According to Dervichian's theory, the change in area from the kink-point (ca 20.5 \AA^2) to the collapse point (ca 18.5 \AA^2) is accompanied by a progressive tilt of the molecules to the vertical position (*e.g.* with stearic acid from the B-form with $\beta = 63^\circ$ to the vertical form with $\beta = 90^\circ$). Careful measurements would then be expected to show a change in compressibility at the latter point, corresponding to the compressibility of the close-packed, vertically orientated hydrocarbon chains. No such change has, however, been observed, and films at smaller areas seem invariably to be partially collapsed.

(9) Harkins and Nutting²⁹ have studied the energy changes involved when crystals of myristic and pentadecylic acids spread to the monolayer on a dilute acid substrate. With myristic acid the plot of the internal latent heat (*i.e.* the latent heat of spreading corrected for the work done by the film in expanding) against the molecular area is linear within the

²⁶ Stenhagen, *Trans. Faraday Soc.*, 1938, **34**, 1328.

²⁷ Bernstein, *J.A.C.S.*, 1940, **62**, 374.

²⁸ Adam, Danielli and Harding, *Proc. Roy. Soc., A*, 1934, **147**, 491.

²⁹ Harkins and Nutting, *J.A.C.S.*, 1939, **61**, 1702.

experimental error. This result appears difficult to reconcile with Dervichian's hypothesis, since the areas considered included condensed, intermediate and expanded films, and different modifications in the monolayer might reasonably have been anticipated to produce discontinuities in the above curve.

(10) Upon metal surfaces, where the polar group faces the metal, electron diffraction measurements by Storks and Germer³⁰ show that the first layer of stearic acid or barium stearate is vertically orientated and irregularly arranged. These authors remark: "It seems probable that this absence of ordered arrangement in the first layer on metal surfaces is accounted for by the fact that the molecules are anchored to the surface by their chemically active ends." The very polar water surface should exert a closely analogous effect.

From these various points it seems reasonable to conclude that Dervichian's theory as quoted above is, in general, incorrect. In the next section practically all known condensed films are examined in the light of the above theories.

2. The Detailed Structure of Certain Condensed Films.

This section deals particularly with those compounds for which a reasonably detailed monolayer structure can be put forward, but also aims at being comprehensive by discussing examples where this is not yet possible. It includes all compounds giving condensed films, except those of rather complex structure, such as the sterols, porphyrins, and other biological compounds. Most attention is given to compounds studied both by force-area and surface potential methods. Any general deductions which can be made regarding the structure in the XY and YZ regions will be given in a later publication.

(1) Ureas, Amides, Acetanilides, Aldoximes, Unsubstituted and α -Amino Acids.

These are classed together since, as already pointed out,³¹ it would seem that their monolayer behaviour is largely determined by cross hydrogen bonding. In the case of the ureas, acids and methyl stearamide it was concluded that their rather large limiting areas of 24-26 Å² were determined entirely by the spatial arrangement of the head-group necessitated by such hydrogen bonding. With the α -amino acids, aldoximes and the high area condensed form of the acetamides it was suggested that at the limiting area cross linkage occurs through the OH bond of a single water molecule. It was also pointed out that cross hydrogen bonding tended to bring about solidification in the monolayer, well shown by the ureas, α -amino acids, and by the low area form of the acetamides. In all cases examined by surface potentials the moment μ appeared to be a maximum at the area best consistent with maximal cross hydrogen bonding.

(2) Methyl Ketones.

These ketones resemble the esters in giving definite evidence of reorientation on compression from the expanded to the condensed state.

³⁰ Storks and Germer, *Physical Rev.*, 1939, **55**, (ii), 648.

³¹ (a) Alexander and Rideal, *Nature*, 1941, **147**, 541; (b) Alexander, *in the press*.

In the expanded region the apparent surface moment μ is 390 milli-Debyes, and this has been reduced to 258 at about 19 \AA^2 in the condensed films.²⁸ The structure in the expanded films is undoubtedly with the dipole vertically orientated in the surface (Configuration I, Fig. 2) as suggested theoretically by Mitchell³² and supported by experiments upon expanded ester films.²⁰ At the limiting area of about 22 \AA^2 in the condensed state the surface potentials indicate that, if the head-group and chains lie in one plane as indicated, then the latter are tilted at close to $26\frac{1}{2}^\circ$ to the vertical, as shown in Configuration II (*cf.* esters below), since taking the $\text{C}=\text{O}$ moment as 390 milli-Debyes (from the expanded films), then the calculated vertical component is 268 milli-Debyes, the experimental 270. On compression the tilt is decreased and μ decreases further, until close-packed vertical chains, necessarily involving some head-group distortion, are obtained at about 20 \AA^2 (Configuration III).

It appears from the minimum value of μ quoted (ca 258 milli-Debyes) that Configuration IV is never obtained, although this gives the simplest

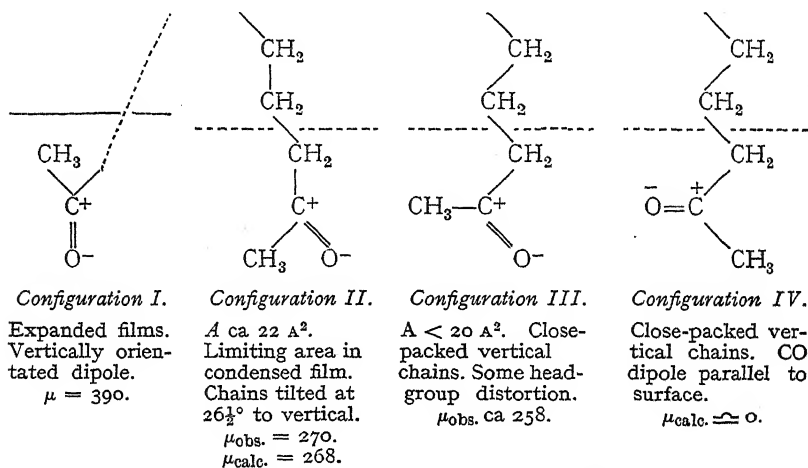


FIG. 2.—Water surface parallel to the horizontal dotted line. Values of μ in milli-Debyes.

molecular packing, since this would have an approximately zero moment. The explanation of the non-occurrence is probably due to energy considerations, since it involves a very considerable distortion (ca 90°) of the stabilising dipole away from its position of minimum energy normal to the surface and, unlike the acetamides, no cross hydrogen bonding is possible to stabilise such a form.

(3) Acetates, other Esters, Glycerides and Lactones.

Acetates and Esters.—The head-group configurations for condensed monolayers of octadecyl acetate, ethyl stearate, cetyl palmitate and cetyl propionate have been worked out in detail.²⁰ With the acetate, palmitate and propionate this required the long-chains to be inclined at close to $26\frac{1}{2}^\circ$ to the vertical at the limiting area X, but with ethyl stearate vertical orientation was necessary to account for the observed moment. The greater stability of the methyl ester

³² Mitchell, *Proc. Roy. Soc., A*, 1936, **155**, 696.

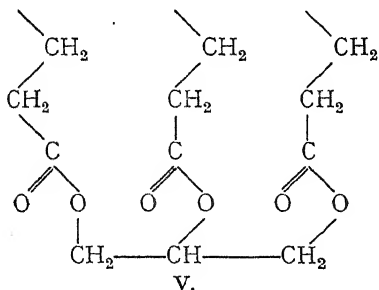
$C_{33}H_{67}COOCH_3$ as compared with the acetate $C_{30}H_{61}OCOCH_3$, previously pointed out by Adam and Dyer,²³ is also in agreement with the structures put forward for these head-groups.

Compression of the condensed acetate monolayers is seen to decrease μ quite rapidly, probably due to a similar reorientation as in the methyl ketones owing to their very similar head-groups. As with the methyl ketones, and for the same reason, the acetates seem to be unstable in the YZ region. The moment of the acetate is ca 455 milli-Debyes at 20 \AA^2 , those calculated for configurations similar to III and IV of Fig. 2 being 480 and 140 respectively. This definitely excludes the latter and shows that the former must be somewhat distorted, both in exact agreement with the conclusions drawn from the methyl ketones. The non-appearance of a configuration similar to IV is explained similarly.

The structure of ethyl stearate at X has now to be considered. Tilted chains as in the acetates seem to be definitely excluded, since the calculated values for the four possible configurations with the chains tilted at $26\frac{1}{2}^\circ$ to the vertical are 277, 80, 7 and -139 milli-Debyes, whereas the vertical configuration gives 198, in good agreement with the experimental range of 200 at X to 190 at Y. A study of a model of the suggested head-group configuration (²⁰ Table III, Fig. 2) indicates, however, that this would occupy an area rather greater than that of close-packed, vertical chains, and it is to this that the observed difference of about 2 \AA^2 between the areas at X and Y is now ascribed.

Triglycerides.—These give the usual type of F — A curve, as shown in Fig. 1, but owing to their much more complex head-groups, no such detailed picture can be put forward as for the simple esters given above. Two facts can be noted, however: firstly, that the surface moment μ only decreases slightly on transition from the expanded to the condensed state (*cf.* ethyl palmitate where μ falls from ca 540 to under 200 milli-Debyes); and, secondly, that no further marked fall occurs over the XY region in the condensed state.^{33, 34} This must mean that the head-

group configuration is almost the same at all areas, and the small value of ca 330 milli-Debyes per ester residue indicates a configuration closer to the "trans" than the "cis". This, of course, would be anticipated from the expected configuration, approximately V (see also reference ²⁵). As with ethyl stearate, this requires an area somewhat greater than that of close-packed hydrocarbon



chains, and so once again it appears to be the packing of the head-group which determines the cohering point area X.

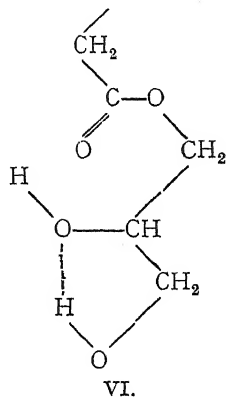
The very similar glycols, such as glycol distearate, closely resemble the triglycerides in their monolayer behaviour.

Diglycerides.—The force-area and surface potential characteristics of α - α' dipalmitin³⁵ show a very similar behaviour to tripalmitin, so a similar explanation of the area at X seems justifiable.

³³ Hughes, *Biochem. J.*, 1935, **29**, 430.

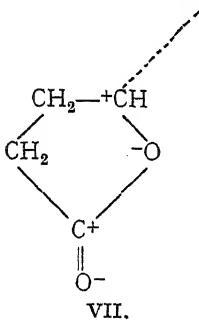
³⁴ Dervichian, *Thesis*, Paris, Masson, 1936.

α -Monoglycerides.—With the α -monoglycerides X has the rather large value^{39b} of 26.3 \AA^2 ; α -monopalmitin shows a very large fall in μ from about 300 milli-Debyes in the expanded region ($A = 60 \text{ \AA}^2$) to about 185 at 26 \AA^2 , and a further fall to about 160 at 20 \AA^2 in the condensed region.³⁵ These decreases indicate head-group re-orientation, and point to the packing of the head-groups as determining the value of X in this case. The rather high value of ca 26 \AA^2 may possibly be due to ring formation by the free alcoholic groups, the suggested configuration being then VI.



Such a structure would account for the comparatively small moment in the condensed state, and by analogy with other ring structures, such as the benzene derivatives and the lactones, would occupy about the observed area. Also from the discussion of the isomeric dihydroxy behenic acids given below it would seem a rather probable suggestion.

Lactones.—The limiting area of the condensed film³⁶ is about 29 \AA^2 , a very reasonable value if due to the close-packed head-groups, since the rather similar *p*-alkyl cyclohexanols give an almost identical area.³⁷ The surface potential measurements of Fosbinder and Rideal³⁸ give for μ at the limiting area a value of 420-440 milli-Debyes. This approaches the value of about 500 milli-Debyes found in the acetates, and points to the resultant dipole being orientated approximately normally to the surface, as in the suggested configuration VII. No marked re-orientation of the head-group can occur on compression as supported by the constant value of μ down to about 23 \AA^2 , where collapse would be expected to set in.



Pentaerythritol Tetrapalmitate.—This provides a very good example where, owing to its nature, it seems most certain that the head-group determines the limiting area²³ of about 100 \AA^2 . Increasing F to 20 dynes decreases this

to 80 \AA^2 (*i.e.* 20 \AA^2 per chain), evidently with close-packed chains.

(4) Benzene Derivatives and Related Compounds.

Simple *p*-substituted benzene derivatives, such as the phenols, anilines and anisoles give identical F - A curves of limiting area³⁹ ca 23.8 \AA^2 . The constancy of this value, its approximation to that expected from X-ray data, and the coefficient of compressibility which is only slightly greater than that of benzene in bulk,³⁹ all point to the limiting area X being determined by close-packed phenyl groups. Further confirmation is given by surface potential measurements of

³⁵ Alexander, *unpublished results*.

³⁶ Adam, *Proc. Roy. Soc., A*, 1933, **140**, 223.

³⁷ Adam, Danielli et al., *Biochem. J.*, 1932, **26**, 1233.

³⁸ Fosbinder and Rideal, *Proc. Roy. Soc., A*, 1933, **143**, 61.

³⁹ (a) Adam, *ibid.*, 1923, **103**, 676; (b) Adam, Berry and Turner, *ibid.*, 1928,

p-hexadecyl phenol which show only a slight fall in μ over the whole region.³⁵ It is of interest to note that the value so obtained (246 milli-Debyes at 23 Å²) is rather greater than that for the alcohols (ca 220 milli-Debyes at 22 Å²), in agreement with the usual observation that the surface moment μ runs parallel to the dipole moment as normally measured.

The two forms of acetanilides observed by Adam³⁹ have been explained on the basis of hydrogen bonding.³¹ With the anilides, of which stearic has been examined in detail by Rideal and Mitchell,^{40(a)} the limiting area of ca 33 Å² appears to be due essentially to the head-group packing consistent with the maximum surface moment, since μ falls considerably on compression.

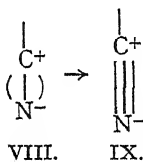
The areas observed with more complex oxygenated derivatives of benzene, such as ca 28 Å² with the acyl resorcinols,⁴⁰ can also be ascribed to the area taken up by the head-groups.

The *p*-alkyl cyclohexanols behave very similarly to the simple *p*-substituted benzene derivatives with a rather larger limiting area³⁷ of ca 30 Å², again most readily ascribed to the head-group packing. As a limiting case where this head-group packing is the determining factor, certain sterols, *e.g.* cholesterol, might be given. Here the agreement between the observed area and that calculated from a molecular model is very good, and again μ shows only a slight decrease on compression.³⁷ However, in this particular case, it would seem more reasonable to regard the sterol skeleton as forming part of the hydrophobic portion, when such monolayers would be regarded as showing only the YZ region. Simple benzene derivatives, such as the phenols, anisoles and anilines given above, may also be considered from a similar view-point.

(5) Cyanides.

In the expanded state the surface moment μ is⁴² about 320 milli-Debyes, and in the condensed 460 at 27 Å², which at first appears to indicate that the dipole is tilted in the former region, in direct contradiction to the theory outlined above. The very high compressibility of the condensed films (6.2×10^{-3} cm./dyne), which is very close to that of the acetates (8.5×10^{-3} cm./dyne), shows that either the tilt is changing or the polar head-group is being compressed. From the parachor measurements (64 for CN as compared with 39 for CH₂), it would appear that the cyanide group is comparatively large, so the limiting condensed area of 27 Å² would seem a reasonable size for this head-group.

The explanation suggested to account for these apparently anomalous moments is that in the expanded state the dipole is vertically orientated as usual; in the condensed the bulky CN groups are close-packed side by side with considerable distortion. This distortion, which begins on transition from the expanded to the condensed state (see the curve for margaric cyanide, *ref.* ⁴², p. 107), results in an extension of the triple bond with a consequent increase in moment. A simple pictorial representation is given by the transition of VIII to IX.



⁴⁰ Adam, *Proc. Roy. Soc., A*, 1928, 119, 628.

^{40(a)} Rideal and Mitchell, *ibid.*, 1937, 159, 266.

⁴¹ Adam, Askew and Danielli, *Biochem. J.*, 1935, 29, 1786.

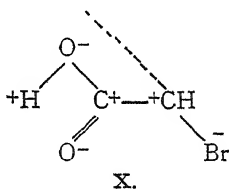
⁴² Adam and Harding, *Proc. Roy. Soc., A*, 1933, 143, 104.

This increase in μ can proceed until the long-chains are close-packed at an area of about 24.5 \AA^2 (i.e. $20/\cos 35^\circ$, taking the hydrocarbon cross-section as 20 \AA^2), but at smaller areas the long-chain packing tends to decrease μ by tilting the dipole away from its position normal to the surface. It is probably the opposition of these two opposing factors which accounts for the almost constant value of μ in the condensed films (i.e. $< 27 \text{ \AA}^2$). In agreement with this suggestion the product μA remains approximately constant from the transition point (33.5 \AA^2) down to about 25 \AA^2 , as it should do if only the length of the dipole were changing.

Finally, if the dipole were tilted in the expanded state, then the value of μ at the limiting area would be expected to vary with the chain-length, whereas it does not (the experimental values being 310, 330 and 320 milli-Debyes for the C_{14} , C_{16} and C_{17} members respectively).

(6) α -Bromoacids.

Only α -bromo-stearic acid appears to have been examined by both force-area and surface potential methods.²⁵ On compression from the limiting area of ca 33 \AA^2 μ decreases from ca 295 milli-Debyes to ca 260 at 28 \AA^2 ($pH 2$ substrate), indicating that at the limiting area the head groups are close-packed so as to produce the maximum change in surface potential. An approximate representation, as previously suggested,⁴³ may be X, with perhaps some interaction between the hydrogen and bromine atoms in neighbouring molecules. A study of the moment in expanded films would indicate if any cross hydrogen bonding does actually occur in the condensed films. Examination of a molecular model shows that the above configuration would require an area of the right magnitude.



(7) Alcohols.

Nutting and Harkins¹⁴ have made very accurate $F-A$ measurements upon the long-chain primary alcohols (estimated error $\pm 0.25 \%$). For the C_{15} – C_{18} members all the limiting areas X lie very close to 21.9 \AA^2 , the kink points Y lying between 20.4 and 20.7 \AA^2 . Assuming vertical chains at Y,⁴⁴ then tilted chains at an angle of $26\frac{1}{2}^\circ$ to the vertical would require areas between 22.8 \AA^2 and 23.1 \AA^2 . In view of the accuracy of the measurements, this definitely rules out tilted chains as the factor responsible for determining the limiting area X.

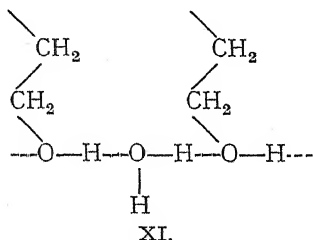
From the surface potential measurements,^{28, 45} it appears that μ increases somewhat from ca 210 milli-Debyes at the limiting area in the expanded state to ca 245 at 22 \AA^2 (i.e. at X), and then falls over the condensed region to ca 215 milli-Debyes. With the alcohols no direct cross hydrogen bonding is possible since the minimum distance of approach is limited to about 4.5 \AA by the hydrocarbon chain packing, but it can be suggested that the limiting area is determined by linkage through the OH bond of a single water molecule, as shown in XI.

⁴³ Alexander, *J. Chem. Soc.*, 1938, 729.

⁴⁴ Alexander, *a subsequent publication*.

⁴⁵ Marsden and Schulman, *Trans. Faraday Soc.*, 1938, 34, 748.

A very similar idea had been suggested earlier to explain certain results with the acetamides and α -amino acids.³¹



Such cross linkage would be expected when the hydrogen bonding between the head-groups exceeds that between the water molecules, as is certainly true for the alcohols.⁴⁶ Another point in favour of the above is that it provides an explanation for the unexpectedly high expansion temperatures of the alcohols ($T_{\frac{1}{2}}$ $C_{16}H_{33} \cdot CH_2OH$ is 54° —cf. Table I of reference ^{31a}).

(8) *n*-Amines.

An explanation similar to that for the alcohols may also be suggested for the amines. No potential measurements have been made upon unionised amines in the expanded state, but as with the alcohols μ falls over the condensed region.⁴⁵ Also the half-expansion temperature approaches that for the alcohols (e.g. 48° for $C_{16}H_{33} \cdot CH_2 \cdot NH_2$).

(9) Unsaturated Acids and Alcohols.

A number of these have been examined by both force-area and potentials in the monolayer by Marsden and Rideal,¹⁷ and as multilayers by the author.¹⁸ With the *cis* and *trans* unsaturated compounds the latter tended to give the more condensed films, and the observed differences in behaviour could be ascribed to the greater ease of packing of the long chains in the *trans* compounds.

The large limiting areas of 28.7 \AA^2 observed by Adam³ for *iso*-oleic acid and ethyl *iso*-oleate can be explained similarly, although since the double bond can be regarded as forming part of the head-group (as shown by the difference in μ from that of oleic acid), they may equally well be due to the head-group packing. With *iso*-oleic acid the surface potential measurements of Hughes⁴⁷ show that μ is a maximum at the limiting area (given as 26.4 \AA^2).

(10) Dihydroxy Acids.

An explanation for the difference in monolayer behaviour between the so-called *cis* and *trans* isomers of 9:10 dihydroxy behenic acid has been suggested by Davies.⁴⁸ The two hydroxyl groups were assumed to be associated by hydrogen bonds in both cases, and the difference was put down to the much greater ease of packing of the chains in the *trans* compound.

(11) Methyl Ethers.

Only octadecyl methyl ether has been studied by both force-area and potential methods.^{11, 45} It gives rather unstable monolayers with the usual type of F — A curve, as given in Fig. 1, the area at X being about 21.5 \AA^2 . Both the F — A and μ — n curves appear to be independent of pH over the range 2 to 10.5; μ falls from 234 to 217 milli-Debyes over

⁴⁶ See Pauling, *The Nature of the Chemical Bond*, Cornell, 1939.

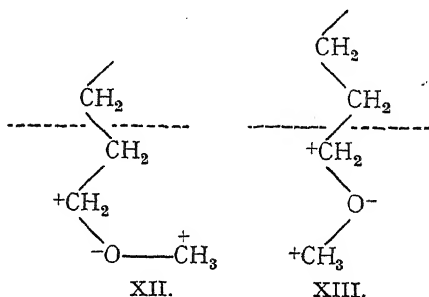
⁴⁷ Hughes, *J. Chem. Soc.*, 1933, 338.

⁴⁸ Davies, *J. Chem. Physics*, 1940, 8, 577.

the condensed region. The kink-point area is close to 19 \AA^2 , so tilted chains at $26\frac{1}{2}^\circ$ would correspond to an area of about 21.3 \AA^2 . The structure suggested at X is shown in Configuration XII, corresponding, at any rate approximately, to such a tilted-chain structure. Measurement of μ in the expanded ether films would, of course, provide a check. Once again, as in the acetates and methyl ketones, and presumably for the same reason, it is seen that the arrangement with the simplest packing (Configuration XIII) does not appear, since this would be expected to show a μ value close to zero. In the most compressed YZ region the configuration is probably one with vertical chains and some head-group distortion, since there is no evidence for any transition to Configuration XIII.

Hence for the ethers a tilted chain structure would seem to be the best explanation for the limiting area X.

The above appears to include all published examples of condensed monolayers except those of the more complex compounds, such as sterols, resinols, porphyrins, etc. An examination of the results shows certain generalisations which will be discussed in a forthcoming publication.



Summary.

PART I.

This consists of a brief review and discussion of the various theories advanced to explain the force-area and surface-potential curves and the physical states given by condensed monolayers. In particular the recent theory of Dervichian which seeks to draw a very close analogy between two and three dimensional structures is critically examined and numerous objections raised against its general validity. From these points it would seem that no such correlation is to be expected, and recent results on the force-area curves and upon the physical states as shown by surface viscosity measurements, are in agreement with this.

PART II.

Concentrating particularly upon those compounds examined by both force-area and surface potential methods, practically all known condensed monolayers are discussed in relation to the theories given in Part I. Attention is focussed upon the packing of the head-groups and long-chains, and upon the orientation of the resultant dipole as indicated by the surface potential measurements. In certain cases a reasonably definite monolayer structure can be advanced. Generalisations from these results will be discussed in a separate publication.

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REVIEWS OF BOOKS.

ANNUAL REPORTS ON THE PROGRESS OF CHEMISTRY, Vol. XXXVII.
1940. (The Chemical Society.) Pp. 525.

In days of peace these reports are always received with pleasure, but now that so many of us are engaged in unusual and often very restricted occupations they are more than usually welcome. They are unique, in that in no other single volume can we find in assimilable form a review of most of the work which interests us. True, we might study British Chemical Abstracts every month, but, for ourselves, we find that condensation has gone to such extremes that such study savours too much of solving cross-word puzzles without the variety of intellectual stimulus which Torquemada provides; and so we use the Abstracts solely as an annotated index.

The year under review saw the temporary passing of much of civilised Europe into intellectual oblivion under the heel of the barbarian. In consequence much that might have been available for report stopped suddenly short in mid-year. It will be interesting, when civilisation has prevailed, to see whether those savants who were unable to escape to freedom have been able to continue work and, if so, whether the fruits of their labours have been acknowledged or whether these too have been stolen to bolster up the pretence of barbarism to be civilised.

In almost every page of the volume under review there is matter of interest to the physical chemist and, by way of change, one can rejoice in the beauty of some of the extraordinary syntheses in which the organic chemists have been engaged. The section entitled "General and Physical Chemistry" occupies 103 pages; it includes an admirable report by Orr on Intermolecular Energies and a full review by Sutton of Electron Diffraction by Gases and Vapours, Dipole Moments, and Atom Polarisation and their application to the study of Molecular Structures, in addition to an article by Ritchie on Kinetics and Photochemistry and a report by Lawrence on Colloids, which deals with Micellar Colloids, Emulsions, Viscosity, Gelation and Thixotropy—all subjects which are constantly recurring in these *Transactions*.

Inorganic chemistry, over the names of Emeléus and Welch, deals mainly with the Boron Hydrides and the Separation of Isotopes by Thermal Diffusion. Practically the whole of the 30 pages devoted to Crystallography are devoted to matters familiar to readers of these *Transactions*: Crystal Physics, Thermodynamics and Structure by Ubbelohde, Hindered Rotation about Single Bonds by Speakman, and Inorganic and Organic Structures by Hampson and J. M. Robertson respectively. The report on Organic Chemistry occupies 190 pages, almost every one of which shows that the organic chemist of to-day is essentially a physical chemist; 30 pages are devoted to a report by Henshall and Smith (though for the last six page headings Smith seems to have been forgotten!) on Aliphatic Compounds, the earlier pages of which serve to advance the study of a recent General Discussion of this Society. Watson on Reaction Mechanisms and Hey on Free Radicals are further reports of particular interest.

In the report on Biochemistry the articles of Neuberger on Proteins, of Danielli on Physicochemical Phenomena and of Bell on Biological Catalysis deserve special mention.

The modern analytical chemist is not, as the popular novelist would have us believe, sufficiently equipped with a set of reagent bottles, a rack of test tubes and a retort; he, too, is a physical chemist in large measure. The report on Analytical Chemistry occupies 27 pages, devoted, *inter alia*, to Fractional and Molecular Distillation (with a useful summary of Azeotropy) and Electrolytic Analysis.

The volume is admirably indexed and excellently produced. The only two "jars" the reviewer received on reading it were the use of the word "placing" as a noun (which caused him to re-read the sentence in which it occurred before it could be understood) and the wholly unnecessary addition of the plural "s" to abbreviations; "cal." is equally applicable to one or to several calories.

Electromagnetic Theory. By J. A. STRATTON. Pp. 615. (McGraw-Hill, New York and London, 1941.) 42s.

The subject of this book is pre-electron classical theory. No mention is made of electron theory, atomic theory or quantum theory. Consequently such phenomena as the Hall effect, thermionic emission, Zeeman effect and Stark effect lie outside the scope of the book, as do the dependence of electric and magnetic properties on temperature.

The first two chapters are devoted to the general theory of electromagnetic fields, the next two to steady states (electrostatic and magnetostatic fields) and the remaining five chapters to electromagnetic waves. On the last subject the book will be found outstandingly useful.

The treatment throughout is advanced, in fact very advanced and in certain respects too advanced. The reader is assumed to have followed an intermediate course terminating in a formulation of Maxwell's equations. This book accordingly begins with a bare statement of Maxwell's equations. These are regarded as postulated relations between the four electromagnetic field vectors E , B , D , H , and all we are told on page 1 about the physical significance of these four vectors is that "eventually they must be defined in terms of the experiments by which they can be measured." This way of beginning is perfectly acceptable in an admittedly advanced book, but what is intolerable is that the reader has to wait until page 96 before he is told the physical significance of any of the field vectors. In the interval he is given a fairly stiff course including electromagnetic potentials, generalised co-ordinates, orthogonality, tensor calculus and special relativity, the need for much of which is not altogether apparent. If the reader is expected to swallow all this without knowing the physical meaning of the field vectors, he is more than likely to suffer from mental indigestion. If, alternatively, it is assumed that he really knows their physical meaning, it is ludicrous to ask him to feign ignorance for nearly a hundred pages.

In many other respects the book is outstandingly good. The thorough treatment of wave propagation has already been mentioned. This is probably the first book in English in which the rather tricky subject of magnetic energy is treated at all adequately.

The author is particularly to be congratulated for consistently using the metre-kilogram-second-coulomb system of units. The reviewer is amongst those who look forward to the day when the e.m.u. beloved by teachers, but never really used by anyone else, will be confined to oblivion. But before that happy day can come, those of us who welcome the M.K.S. system must agree amongst ourselves. Unfortunately there appears to be not one M.K.S. system, but four, or rather two pairs. The alternative versions are summarised in the table below. The author uses the rational

	Rational.		Irrational.	
	I	II	I	II
Definition * of M	$\mu_0 M = B - \mu_0 H$	$M = B - \mu_0 H$	$4\pi\mu_0 M = B - \mu_0 H$	$4\pi M = B - \mu_0 H$
Value of μ_0 in henry/metre	$4\pi \times 10^{-7}$ weber metre ²	$4\pi \times 10^{-7}$ weber metre ²	10^{-7} weber metre ²	10^{-7} weber metre ²
Unit of B	$\frac{\text{amp. turn}}{\text{metre}}$	millioersted	$\frac{\text{amp. turn}}{\text{metre}}$	millioersted
Unit of H	$\frac{\text{amp. turn}}{\text{metre}}$	$\frac{\text{weber}}{\text{metre}^2}$?	?
Unit of M	$\frac{\text{amp. turn}}{\text{metre}}$	$\frac{\text{weber}}{\text{metre}^2}$?	?
Unit of magnetic moment	amp. turn metre ²	weber-metre	?	?

* M denotes magnetic moment per unit volume or intensity of magnetisation. B and H have their usual significance.

set I and refers to the alternative irrational (surely a better word than "unrationalised") set I. A recent book entitled "M.K.S. Units and Dimensions," by Jauncey and Langsdorf (Macmillan, 1940), on the other hand, describes in detail the irrational set II and refers briefly to the alternative rational set II. Thus, quite apart from the recognised choice between rational and irrational units, here are two books both published in the past year, one using set I, the other set II. So far as the reviewer knows, set II is the more usual, but he nevertheless on the whole prefers set I. He is therefore not worried by Professor Stratton's choice of set I, but he is intensely worried by the fact that he does not even mention the existence of the alternative II. Does this mean that Professor Stratton was not aware of the difference? The first step towards uniformity must be a recognition that sets I and II are different, that both are permissible according to the chosen definition of M . Any question of one being "right" and the other "wrong" is nonsense. Only when this is recognised, can the question, which is the more useful, be profitably attacked.

E. A. G.

CORRIGENDA.

Page 299, equation (3), substitute $m(m+1)$ for $m(m-1)$.

„ 300, bottom line „ $20-p'r_e$ for $20-p'r_e$.

„ 301, equation (6) „ $T = kn^{\frac{5}{3}}V^{-\frac{2}{3}}$ for $T = kn^{\frac{5}{3}}V^{-\frac{2}{3}}$.

equation (9) „ $2kmn^{\frac{5}{3}}$ for $2kmn^{\frac{5}{3}}$.
(right hand numerator)

„ 302, line 3 „ $m = 6$ for $m \times 6$.

„ 7, delete "only".

Annual General Meeting

NOTICE IS HEREBY GIVEN that the ANNUAL GENERAL MEETING of the Society will be held at the HOTEL REMBRANDT, Thurloe Place, London, S.W. 7, on FRIDAY, 26th September, 1941, at 9.45 a.m.

G. S. W. MARLOW,

Secretary.

6 GRAY'S INN SQUARE,

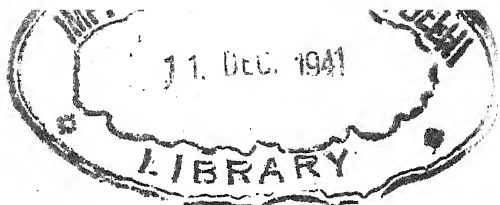
GRAY'S INN, W.C. 1.

Tel.: Chancery 8101.

August, 1941.

NOTICE

THE Society's Office will be CLOSED from MONDAY, 4th August, until SATURDAY, 16th August inclusive, but communications with regard to papers for publication can be sent to the Editor, at 4 Hillcrest Road, London, S.E. 26.



THE EFFECT OF SOME ORGANIC DYE IONS ON THE ELECTROKINETIC POTENTIAL AT THE GLASS WATER INTERFACE.

BY D. O. JORDAN.

Received 22nd April, 1941.

The variation of the electrokinetic potential (*i.e.* the ζ potential) at the glass water interface with the addition of dissolved substances has been investigated by several authors using the streaming potential method.^{1, 2, 3, 4} This variation is complicated by the dependence of the potential on the charge per sq. cm. of the diffuse layer (e), and on the thickness of the diffuse layer (d), a variation in the ζ potential being caused by a change in the value of either d or e or most probably by a variation in the values of both. With the addition of univalent inorganic cations the ζ potential at first increases with increasing concentration of the electrolyte. Freundlich⁵ suggested that this increase is due to the adsorption of the anion and terms it the "charging" effect. Bull and Gortner,⁶ using an inert surface of cellulose, however, have shown it to be due to an increase in d . At greater concentrations the potential slowly decreases or is discharged by the adsorption of the cation. With increasing valency the initial increase in the ζ potential becomes less marked, and with trivalent and quadrivalent cations the adsorption is sufficiently strong to reverse the sign of the charge at the glass surface. According to Rutgers⁷ the initial maximum observed by these authors^{1, 2, 3, 4} is due to the fact that in determining the ζ potential the value of the specific electric conductivity used was that of the solution in bulk and not that of the solution in the capillary, and he considers that the potential should fall gradually with increasing concentration. Various investigators^{6, 8, 9, 10} had previously shown that when using dilute solutions the surface conductance has an appreciable value, which varies with the radius of the capillary.

There are few references in the literature to the effect of organic ions on the electrokinetic potential at the solid-liquid interface. Von Elissasoff¹¹ has studied the effect of picrate ions, and also of the anions

¹ Kruyt, *Kolloid Z.*, 1918, **22**, 81.

² Freundlich and Rona, *Sitz. Preuss. Akad. Wiss.*, 1920, **20**, 397.

³ Freundlich and Ettisch, *Z. physik. Chem.*, 1925, **116**, 401.

⁴ Furitani, Kurokuchi and Asoda, *Jap. J. Gastroent.*, 1930, **2**, 148.

⁵ Freundlich, *Colloid and Capillary Chemistry*, p. 258.

⁶ Bull and Gortner, *J. Physic. Chem.*, 1931, **35**, 309.

⁷ Rutgers, *Trans. Faraday Soc.*, 1940, **36**, 69.

⁸ Smoluchowski, *Physik. Z.*, 1905, **6**, 529.

⁹ Briggs, *J. Physic. Chem.*, 1928, **32**, 641.

¹⁰ Bikermann, *Kolloid Z.*, 1935, **72**, 100.

¹¹ Von Elissasoff, *Z. physik. Chem.*, 1912, **79**, 385.

of some organic sulphonic acids on the electrokinetic potential at the glass water interface by the method of electro-osmosis. Freundlich and Rona,² and Furitani, Kurokuchi and Asoda⁴ observed that the sign of the charge at the interface was reversed by the addition of basic dyes such as new fuchsine and methyl violet.

It is now generally accepted that many organic dyes in aqueous solution are colloidal electrolytes, and Robinson *et al.*¹² and Valko¹³ have independently shown by measurement of diffusion, electrical conductivity and transport numbers, that in common with other substances belonging to this category, such as the paraffin chain salts, aggregation occurs in aqueous solution to form ionic micelles. Unlike the paraffin chain salts, however, it appears most improbable that micelle formation occurs rapidly at any particular concentration owing to the number and complexity of the polar groups present.

Experimental.

Apparatus.—The use of sintered glass filter plates as suitable membranes for the measurement of streaming potentials was first described

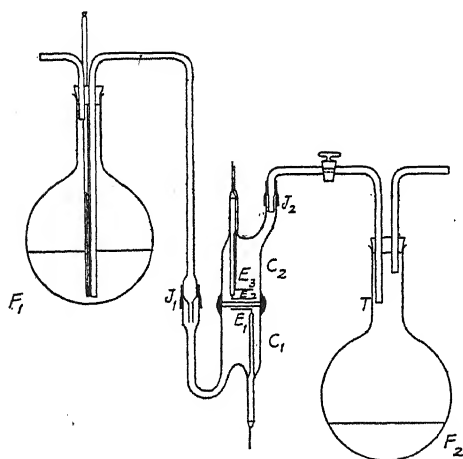


FIG. 1.

by Martin.¹⁴ The diaphragms consist of particles which are almost uniform in size. The importance of this uniformity has been emphasised by Bull and Gortner,¹⁵ who have shown that the streaming potential is a linear function of the hydrostatic pressure only when the particles of the diaphragm are of homogeneous size.

The apparatus used is illustrated in Fig. 1. The sintered glass membrane size G.4, 30 mm. in diameter, was held firmly between the plane ground ends of the two parts of the streaming cell C_1 and C_2 , by means of a clamp (not shown in Fig. 1). The junction of the cell with the

membrane was made air tight by cementing with pure molten paraffin wax, care being taken that the wax did not come into contact with the solution in the cell. The sintered membrane was carefully cleaned between each experiment, first by removing all trace of the paraffin by repeated washing with hot 40°–60° C. petrol ether, followed by treatment with hot chromic-sulphuric acid. The membrane was finally washed, using light suction with approximately 1 litre of hot distilled water followed by 250 c.c. of cold equilibrium water (conductivity 0.8×10^{-6} ohms⁻¹ cm.⁻¹). The rest of the apparatus was cleaned with hot chromic-sulphuric acid followed by boiling distilled water and finally cold equilibrium water.

¹² Robinson, *et al.*, *Proc. Roy. Soc., A*, 1931, **131**, 576, 597; 1934, **143**, 630; 1935, **148**, 681; *Trans. Faraday Soc.*, 1935, **31**, 245.

¹³ Valko, *ibid.*, 230.

¹⁴ Martin, *J. Physic. Chem.*, 1934, **38**, 213.

¹⁵ Bull and Gortner, *ibid.*, 1932, **36**, 111.

The dye solutions were placed in flask F_1 , after the apparatus had been assembled and freed from carbon dioxide by the passage of a stream of purified air. The solution then flowed from F_1 through the cell into F_2 . By means of the junctions J_1 and J_2 it was arranged that the solution did not come into contact with any rubber while passing through the cell. The hydrostatic pressure in F_2 was maintained at about 10 cm. of mercury below atmospheric pressure by means of a constant pressure device. The hydrostatic pressure (P) was measured by the difference in level (h_m) of the two arms of a mercury manometer, and by the height of the liquid (h_w) in F_1 above the outlet into F_2 . Then $P = h_m + h_w/13.55$ at 20° C.

The streaming potential E was measured between electrodes E_1 and E_2 as also was the specific conductivity (including surface conductance) k_s . Electrodes E_2 and E_3 could be used for determining the conductivity k of the bulk of the liquid. The measurement of the streaming potential requires a circuit of very high resistance, an electrometer valve with a Tinsley potentiometer was employed giving an accuracy of 0.2 mv. The resistance between the electrodes was measured by a Mullard resistance bridge, an alternating current of 1000 cycles being used for all determinations.

Before passing the dye solutions through the membrane, pure water (or dilute sodium chloride) was streamed through the cell. A steady potential was obtained after a few minutes. Whilst streaming was continued, the conductivity was determined both through the membrane and in the bulk of the solution. The measurement of resistance necessarily disturbs the ionic arrangement in the diffuse layer and it was found that a short period of time was required to elapse with no movement of the solution before the initial steady value was regained. The dye solution was then placed in F_1 and the dye solution streamed through the membrane until a steady potential was obtained. The specific conductivity across the membrane and in the bulk solution was then determined as before.

Purity of Materials.—The dyes used in this investigation were: new fuchsine (C.I. 678), benzopurpurine 4B (C.I. 448), chlorazol sky blue FF (C.I. 518), congo red (C.I. 370), and orange II (C.I. 151). All were commercial samples and were purified by a similar method to that described by Robinson and Mills.¹⁶ The dye was dissolved in hot distilled water and filtered to remove insoluble impurities, and then precipitated three times from aqueous solution by the simultaneous addition of alcohol and a saturated solution of sodium acetate. The dye was then free from chloride. To remove the sodium acetate and organic impurities the dye was then recrystallised twice from 50 % ethyl alcohol. The absence of acetate was confirmed by a negative result for the cacodyl test. In the case of new fuchsine, which is soluble in alcohol, the dye was freed from insoluble impurities in the same manner and then salted out from aqueous solution by the addition of saturated NaCl. This was followed by two recrystallisations from pure water. The yield was poor but a satisfactory product was obtained.

The dyes were dissolved in hot equilibrium water (or dilute sodium chloride solution), the resulting solution boiled to ensure complete solution and then diluted to the required volume. The solutions were then placed in a thermostat at 20.5° C. for approximately 30 minutes before using. In the case of extremely dilute solutions a small volume of a stronger solution was first prepared and then diluted to the required strength. In all cases the solutions were prepared fresh. The glass used for the preparation and storage of these solutions was always either Pyrex or Hysil.

The temperature of all experiments was 20° C. \pm 0.5°.

¹⁶ Robinson and Mills, *Proc. Roy. Soc., A*, 1931, 131, 576.

Results and Discussion.

Calculations of ζ potential are generally made by the well known formula of Smoluchowski,

$$\zeta = \frac{4\pi\eta Ek_s}{P\epsilon},$$

where ζ = ζ potential, η = coefficient of viscosity, E = observed E.M.F., k_s = specific conductivity of the liquid in the diaphragm including surface conductance, P = hydrostatic pressure, ϵ = dielectric constant. It is general to assume that dilute solutions have the same dielectric constant as the pure solvent and that the dielectric constant in the diffuse layer is also that of the solvent. Bull and Gortner¹⁷ have shown, however, that these conditions are most probably not true and they have introduced the formula

$$de = \frac{\eta k_s E}{P},$$

where d = thickness of double layer, and e = charge per sq. cm. of the double layer, and other quantities have the meaning stated above.

This formula has been used throughout this work. The value of η in dilute solution may be taken as that of water without appreciable error. The product " de " may be regarded as the electric moment of the double layer.

The value of de in pure water varied slightly with the conductivity of the water;^{18,19} the variation of the latter was from 0.7×10^{-6} to 1.1×10^{-6} ohms⁻¹ cm.⁻¹. This variation was reflected in the value of de which varied from 5.0 to 5.5×10^{-4} e.s.u. The initial water value, however, appears to have little effect within limits on the

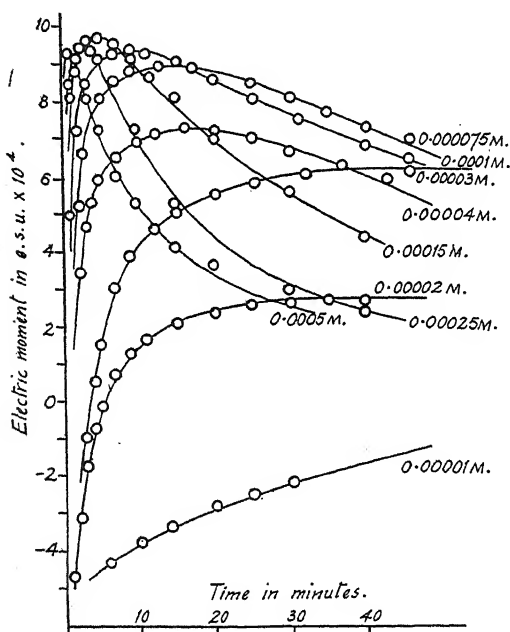


FIG. 2.—Variation of the electric moment with time for solutions of new fuchsine.

final potential obtained in the presence of the dye ions.

The variation of the electric moment of the double layer with time when solutions of new fuchsine are streamed through the glass membrane

¹⁷ Bull and Gortner, *Physics*, 1932, 2, 21.

¹⁸ Abramson, *Electrokinetic Phenomena*, 1934, p. 133.

¹⁹ Lachs and Biczak, *Z. physik. Chem.*, 1930, 148, 441.

is shown in Fig. 2. At low concentrations the value of de falls slowly to zero and then rises to a constant positive value. At higher concentrations the reversal of the charge takes place very rapidly and a maximum positive value is obtained after a few minutes, this value then slowly falls, approaching a constant positive value after 30 minutes streaming. The constant value was, however, only obtained in the most concentrated solutions. The values of de at the maximum value are plotted against the square root of the concentration in Fig. 4, curve 1.

With solutions of benzopurpurine 4B somewhat similar de/t curves were obtained, although in this case there was no reversal of the sign of the charge (Fig. 3). The curves show a rapid increase in moment from the negative water value to a value of the order of -12×10^{-4} e.s.u.; this then gradually falls with time, giving a final constant value which with more concentrated solutions is close to a zero value of the electric moment. Similar results have been obtained with solutions of congo red. Solutions of chlorazol sky blue FF and of orange II did not behave in the same manner but gave a constant value of the electric moment after only a few minutes streaming, thus resembling a true electrolyte. In Fig. 4 the final constant values of

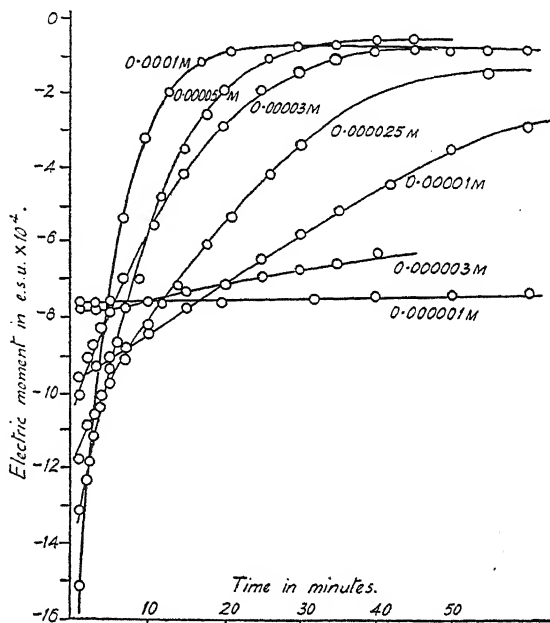


FIG. 3.—Variation of the electric moment with time for solutions of benzopurpurine 4B.

the electric moment for solutions of benzopurpurine 4B (curve 2), congo red (curve 3), chlorazol sky blue FF (curve 4) and orange II (curve 5) are shown plotted against the square root of the concentration. The benzopurpurine 4B and congo red curves exhibit small but sharp minima at very low concentrations and then rise sharply to a constant value of de of approximately -1.0×10^{-4} e.s.u. The chlorazol sky blue FF curve, however, exhibits a large minimum and the decrease of de is very gradual and does not approach zero in any of the solutions studied, although it most probably would at high concentrations where the measurement of the electrokinetic potential is experimentally impossible owing to the high conductivity and very low value of the streaming potential obtained.

It was observed that when solutions of benzopurpurine 4B, congo red and new fuchsine, but not chlorazol sky blue FF and orange II, were being

streamed through the membrane at constant pressure there was a very marked fall in the rate of flow through the membrane. This rate of flow may be measured very conveniently by measuring the time taken for a convenient number of drops to fall from the tube T into the flask F₂ (Fig. 1). If the pressure remains constant then the volume of the drop will be determined by the surface tension of the solution, which will be constant for any given solution. It was found that there was no great variation of the surface tension with concentration in the dilute solutions used, so that the error is not appreciable if it is assumed that the rate of

flow is directly proportional to the time of formation of one drop issuing into the flask F₂. The values for the time of formation of one drop plotted against time for different concentrations of new fuchsine and benzopurpurine 4B are shown in Fig. 5. The values obtained for congo red solutions are very similar to those obtained with benzopurpurine 4B. In the more concentrated solutions the curves rise steeply after only a few minutes streaming whilst in more dilute solutions the variation of the rate of flow with time is small. With solutions of benzopurpurine at concentrations greater than 0.0001 M the flow of the solution through the membrane was almost stopped after 3 minutes streaming and the determination of the electrokinetic potential was impossible. It is im-

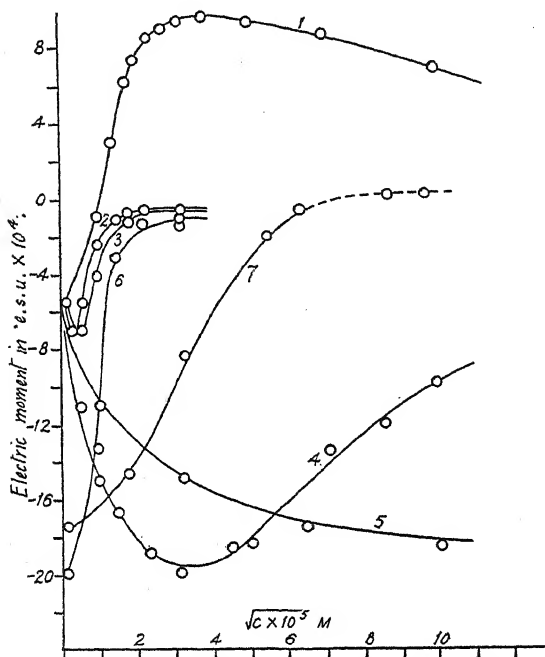


FIG. 4.—Variation of electric moment of double layer with time at the glass water interface in the presence of various dye ions.

1. New fuchsine.
2. Benzopurpurine 4B.
3. Congo red.
4. Chlorazol sky blue FF.
5. Orange II.
6. Benzopurpurine 4B in 0.0001 M NaCl.
7. Chlorazol sky blue FF in 0.0005 M NaCl.

probable that this effect is an electroviscous effect since the equation of Smoluchowski²⁰ states that an increase in viscosity (*i.e.* decrease in the rate of flow) will be produced by an increase in the electrokinetic potential, whilst it is observed that both the rate of flow and the electrokinetic potential decrease simultaneously.

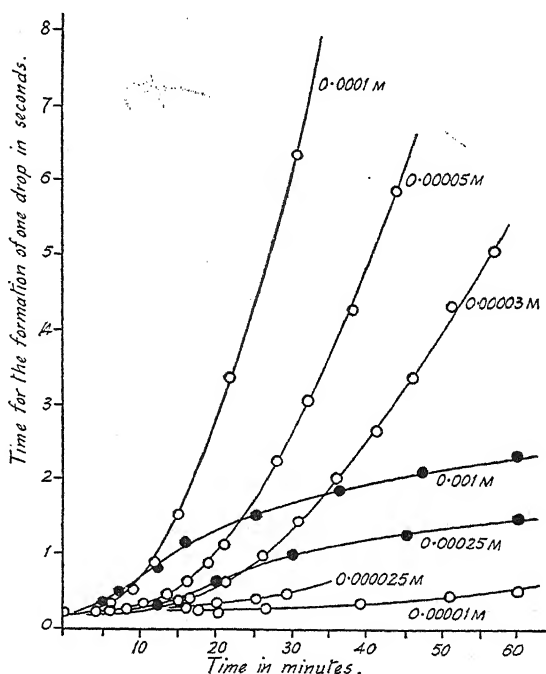
From the microscopic examination of the membrane after an experiment it was apparent that this decrease in the rate of flow was due to the aggregation of the dye at the surface of the glass, thus

²⁰ Smoluchowski, *Kolloid Z.*, 1916, 18, 190.

decreasing the pore size and restricting the flow of the solution. It was thought probable that this clogging of the membrane might be partially or even wholly due to the presence of insoluble matter in the dyes examined. This view was disproved by further purification of a sample of benzopurpurine 4B.

A small quantity of the dye was dissolved in redistilled water and filtered twice through Whatman no. 42 filter paper with light suction, the dye was then precipitated by the addition of filtered alcohol and the precipitated dye filtered off. The dye was then again dissolved in redistilled water and filtered hot first through a sintered glass filter size 3, and finally through a Jena sintered glass filter size 4; this latter stage had to be carried out under high vacuum as the filter rapidly became clogged. This solution was evaporated to dryness on a water bath in Pyrex apparatus, care being taken to exclude dust particles. The dye

FIG. 5.—Variation of the rate of flow with time for solutions of benzopurpurine 4B (○) and of new fuchsin (●).



was dried on the water bath under vacuum, then in an air oven at 105°C . and finally powdered in an agate mortar and dried in a vacuum desiccator over concentrated H_2SO_4 . The variation of de with time and the rate of flow with time for an 0.00005 M solution of the purified dye was then compared with the results obtained previously, the results are shown in Fig. 6, where it is seen that there is little difference between the behaviour of the solutions prepared from the two samples of dye (these results were obtained with a different membrane from that used for the values in Fig. 3, the rate of aggregation being somewhat slower). Filtration of the solution prior to determining the streaming potential, however, produces a marked difference in the values of both de and the rate of flow obtained, as is shown in Fig. 6, curve 3.

The relationship between the rate of flow and the electric moment of the double layer is shown in Fig. 7, where it is seen to be independent

of the dye concentration. At first, over the region of constant rate of flow the lowering of the electric moment is probably due to the adsorption of the sodium ion. The very low value of de finally obtained, however, will be due to the further lowering of the streaming potential

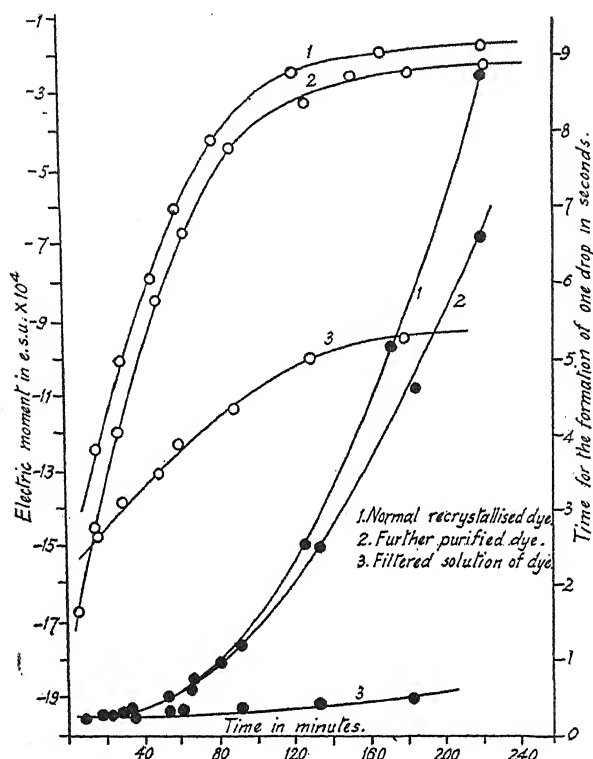


FIG. 6.—Variation of electric moment (○) and rate of flow (●) with time for solutions of 0.00005 M. benzopurpurine 4B.

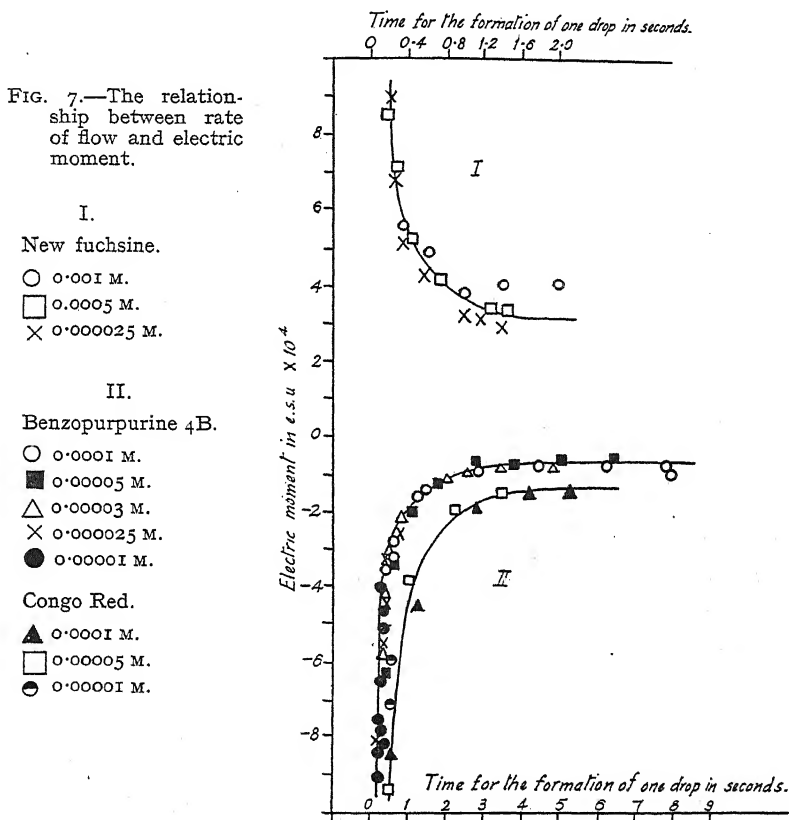
by the effect of the abnormal conditions prevailing in the clogged membrane. In order to investigate these conditions the conductivity through the membrane has been measured and was found to be always greater than the conductivity in the solution. This was observed even when the membrane was partially clogged by the aggregated dye and may be attributed to surface conductance. Some typical results for solutions of benzopurpurine 4B are given in the accompanying table, the membrane being in a clogged condition in the case of the higher concentrations.

Concentration.	$k \times 10^6$.	$k_s \times 10^6$.	$(k_s - k) \times 10^6$.
0.000003 M	1.88	3.10	1.12
0.00001 M	2.94	4.50	1.56
0.000025 M	5.77	7.81	2.04
0.00005 M	8.94	11.80	2.86
0.0001 M	17.54	19.54	2.22

The dye gel present in the glass membrane thus considerably restricts the flow of the solution but apparently does not restrict the transport of ions through the membrane. Under such conditions of

unequal passage of ions and of solution through the membrane the equation of Smoluchowski for the determination of the electrokinetic potential most probably will give incorrect values. Another factor which will contribute to the lowering of the streaming potential in the clogged membrane is the reduction of the pore size of the membrane by the aggregated dye. The existence of a critical pore size, below which the theory of Smoluchowski is inapplicable has been demonstrated by Bull and Moyer.²¹

The dyes which have been shown by Robinson *et al.*¹² and by Valko¹³ to exist in aqueous solution in the form of colloidal micelles are those



which exhibit the property of aggregating at the glass-solution interface and thus reducing the rate of flow of the solution through the membrane. It is suggested therefore that there may be some connection between the condition of the dye in aqueous solution and the aggregation of the dye at the surface of the glass membrane. The effect of the magnitude of the electric moment of the double layer on this aggregation cannot be determined from the data so far obtained.

Two preliminary curves have been obtained for benzopurpurine 4B and chlorazol sky blue FF in sodium chloride solution (Fig. 4).

²¹ Bull and Moyer, *J. Physic. Chem.*, 1936, 40, 9.

Comparison with the results obtained in pure water show that in the case of the former dye there is little alteration in the curve, but with the latter dye a very marked difference in electric moment is obtained; this may be related to the increase in the size of the micelle in solutions of chlorazol sky blue FF in the presence of sodium chloride which has been demonstrated by Valko.¹³

Summary.

The electric moment of the double layer at the glass-water interface has been determined in the presence of five dyes by the streaming potential method.

Coagulation of the dye at the interface has been observed in the case of those dyes known to exist as colloidal micelles in aqueous solution.

Some measurements have been made in the presence of sodium chloride.

I wish to record my thanks to Professor J. Masson Gulland whose encouragement has been much appreciated, and to the Imperial Chemical Industries Ltd. for the loan of apparatus.

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STUDIES IN HYDROGEN OVERVOLTAGE AT HIGH CURRENT DENSITIES. PART V. THE DECAY OF HYDROGEN OVERVOLTAGE.

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The study of the decay of potential at a cathode after interruption of the polarising current might be expected to throw considerable light on the mechanism of hydrogen overvoltage, but the subject has not hitherto been very fully investigated, probably owing to the experimental difficulties involved; it is essential, if the process is to be fully explored, that a measuring apparatus be employed which is able to give accurate instantaneous values of the potential from the moment of switching off the polarising current, and which, moreover, will not take appreciable current from the electrode. In the low current density range (up to 10^{-3} amp./sq. cm.), the most complete study is that of Baars;¹ he used a mirror galvanometer in conjunction with a two-stage amplifier, and by photographing the deflection on a moving film he was able to follow the course of the potential decay from a minimum time of 10^{-3} second after interruption of the current. From observations at Pt, Au, Ag, Cu, Pb, and Hg electrodes, he found that the $\eta - \log_{10} t$ graphs (η — overvoltage, t — time in seconds from interruption of current) were in general straight lines, but for small values of t deviations from linearity occurred; the rate of decay, measured by $d\eta/d\log_{10} t$, was found to vary considerably from metal to metal, and Baars suggested that it was proportional to the value of b in Tafel's

¹ *Sitz. Ges. Beförd. Naturwiss. Marburg*, 1928, **63**, 213.

equation. Armstrong and Butler,² using a Lindemann electrometer as their indicating instrument, also found that the logarithmic relation applied to Hg and Pt electrodes, but their times of observation were comparatively long (> 1 second). Bowden³ has made some isolated observations on the decay of overvoltage, and has pointed out the importance of metallic impurities and oxygen in determining the course of the process in some cases. In the higher current density range the use of the commutator method for measuring overvoltage gave some indication of the rate of potential decay⁴ on interruption of the polarising current, and showed that it could be very rapid and vary considerably for different electrodes. Ferguson and co-workers⁵ have used the commutator or an electromagnetic interrupter in conjunction with a valve amplifier and moving coil oscillograph for the study of overvoltage decay. As a result of extensive work, they arrive at the conclusion that hydrogen overvoltage is made up of two parts, one which drops very rapidly when the charging circuit is opened, while the other decreases only slowly; moreover they suggest that the part of the overvoltage which drops rapidly is the only one which changes appreciably with current density.

The method of potential measurement used by the present authors in the earlier parts of this series⁶ is ideally suited to the study of the decay of polarisation potentials since it permits of the measurement of the instantaneous potential of the electrode at the end of a period of interruption of the polarising current, and this period can be varied from about 10^{-5} second upwards by simple adjustment of resistances in the interrupter circuit; furthermore since the electrode potential is used to operate the negatively charged grid of a thyratron, the current drain on the electrode is negligibly small. In the apparatus as originally constructed⁷ the range of interruption was from approximately 10^{-5} to 20×10^{-5} second, but by rebuilding the apparatus (*vide infra*) the range has been extended and now covers 10^{-5} to 10^{-1} second; for longer periods than this, the polarising current is switched off by hand and the time taken for the potential to reach a value previously set on the thyratron-potentiometer is observed. This apparatus provides, therefore, a direct method for the observation of potential decay from the shortest up to the longest times, and a comprehensive investigation of the decay of hydrogen overvoltage (with polarising current densities of 10^{-3} to 1 amp./sq. cm.) at a wide variety of electrodes has been made with its aid.

Experimental.

The Interrupter.—The modified circuit is shown in Fig. 1, the interrupter embodying the components enclosed by the dotted square. The method of working is as follows. The battery B (72 volt dry battery) charges up the condenser C (0.55 microfarad) through the resistances r_1 (50,000 Ω safety resistance) and r_2 (1 megohm variable resistance),

² *Trans. Faraday Soc.*, 1933, **29**, 1261.

³ *Ibid.*, 1927, **23**, 571; see also Bowden and Rideal, *Proc. Roy. Soc., A*, 1928, **120**, 59.

⁴ Newbery, *J. Chem. Soc.*, 1924, **125**, 511; see also *Trans. Amer. Electrochem. Soc.*, 1930, **58**, 187, for attempts to use the cathode ray oscillograph for studying the decay of overvoltage.

⁵ For a summary of this work, see *ibid.*, 1939, **76**, Preprint 14.

⁶ Part I, *Trans. Faraday Soc.*, 1940, **36**, 1226; Parts II, III, and IV, *ibid.*, 1941, **37**, 224, 319 and 333.

⁷ Hickling, *ibid.*, 1937, **33**, 1540.

and when the condenser reaches a sufficient potential, the thyatron T (Osram GT.5E) flashes over and permits the condenser to discharge through one of the resistances $R_1, R_2, R_3 \dots$, selected by the 20-stud rotary switch S (Muirhead, 5-C-4). This, however, is included in the grid circuit of the triode valve V (two Osram PX25 valves in parallel) which carries the main current,⁸ and the condenser discharge has therefore the effect of imparting momentarily a high negative bias to the grid of the valve and thus preventing the passage of current. The process then repeats itself indefinitely. The voltage at which the thyatron flashes over was adjusted to the maximum voltage of the battery B by means of the biasing unit p , consisting of a 4.5 volt dry battery and a 100,000 Ω potentiometer; b was a 4.5 volt dry battery which served to keep the grid of V slightly negative under all circumstances. The resistances $R_1, R_2, R_3 \dots$ formed a bank of 17 non-inductive resistances such as are used in wireless work. The first of these was a 1000 Ω variable resistance of the circular type equipped with dial; this was mainly used in determining overvoltages in the ordinary way, since by measuring cathode potentials for various settings of the dial and extrapolating to

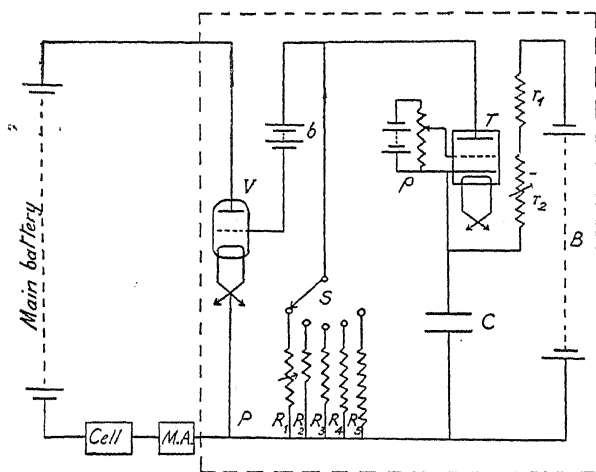


FIG. 1.—Modified interrupter circuit.

0, the overvoltage at zero time of interruption can readily be found without the absolute values of the periods of interruption being known. The remaining resistances, which had values of 25 to 250,000 Ω , were fixed, and served to provide definite periods of interruption over a wide range of times (*vide infra*).

Apart from the extension of the time range, the interrupter is fundamentally the same as that originally described,⁷ but a number of minor improvements, which continual use of the apparatus showed to be desirable, have been made and may be briefly indicated. The thyatron has been placed between the condenser C and the grid, instead of the filament, of V; this obviates any swing of potential of the point P relative to earth when the thyatron trips, and avoids the feeding of any current pulse to the cell which may occur if the resistance to earth of the instrument is low and the capacity of the cell to earth is appreciable. The 1 megohm variable resistance r_2 provides a finer control of the frequency of interruption than was originally available; it is advisable in all cases to keep the time for which the current is on much larger than the period

⁸ The current was changed as desired by varying the input voltage of the transformer which supplied the filaments.

of interruption, so that the milliammeter measuring the current gives its true value and not any mean figure, and this can readily be achieved, even with the longest time intervals, by working at a frequency of interruption of about 1 per second. Finally, it seems in general preferable to have the cell and current meters in the negative, rather than the positive, lead of the main battery.

Calibration of the Interrupter.—The duration of any interruption of current depends upon the time taken for the voltage of the condenser C to drop by a given amount and is therefore directly proportional to the value of the resistance ($R_1, R_2, R_3 \dots$) through which it discharges, if other factors are maintained constant. These other possible variables, which determine the absolute time of interruption, are (a) the capacity of C, (b) the voltage of B, and (c) the grid voltage at which V ceases to pass current (cut-off voltage); (a) is of course constant, and (b) was maintained so; (c) is constant for a given plate potential, *i.e.*, for a steady value of the voltage of the main battery and this was therefore kept at 200 volts; (c) varies, but only slightly, with filament temperature (*i.e.*, when different currents are used). If the values of (a), (b) and (c) are known, the period of interruption can be calculated approximately, but in the present work it was thought desirable to have a direct calibration of the interrupter for each polarising current used, and this was achieved in the following way.

The cell in the circuit was replaced by a condenser shunted by a resistance, part of which was included in the main current path (see Fig. 2), so that the condenser was charged to approximately 1 volt when the current to be used was flowing. The maximum and minimum voltages across the condenser were then measured by the thyatron potentiometer⁹ for all settings of the interrupter. The maximum value V_1 is the voltage when a steady current is flowing, and the minimum voltage V_2 is the value to which the voltage decays at the end of the period of interruption. Hence applying the formula $t = RC \log_e V_1/V_2$, the time of the interruption can be directly found. Using suitable standard resistances and capacities, the time intervals were thus obtained for all settings of the interrupter with currents of 10^{-1} , 10^{-2} and 10^{-3} amp. flowing. To average the values and reduce incidental errors of observation, the times for each current were plotted against the known values of the interrupter resistances $R_1, R_2, R_3 \dots$, and they were found, as expected, to group themselves about a straight line in each case. From these graphs the times of interruption were then read off (Table I). It is to be noted that the time intervals are not very different for the various currents, and for a current of 10^{-4} amp., which it was desired to use in the electrolytic work, it was assumed that they were the same as those for 10^{-3} amp., since in this case the values could not readily be obtained directly.¹⁰

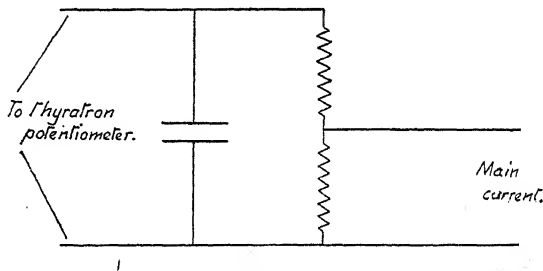


FIG. 2.

The Thyatron-Potentiometer.—This instrument was essentially the same as previously described,⁹ and in conjunction with an ordinary potentiometer-voltmeter gave potential measurements to the nearest 0.005

⁹ Hickling, *loc. cit.*⁷; see also *J. Scientific Instruments*, 1938, 15, 22.

¹⁰ The value of the resistance shunting the condenser was then too high to allow of accurate measurements being made with the thyatron-potentiometer.

volt. By the use of large capacity accumulators for the heating of the thyatron filament, the drift of the balance point could be made very small (less than 0.01 volt in several hours), and this obviated the need for frequent checking during the course of an observation.

It may be useful to mention here two points which have emerged from the constant use of the instrument in conjunction with the interrupter for electrode potential measurements over the past three years: (1) The anode to cathode resistance of the electrolytic cell should not exceed about 1000 Ω . (2) The potentiometer leads should be kept as short as possible and free from inductance to avoid pick-up from the interrupter circuit. If these two conditions are observed, the working of the apparatus is completely satisfactory and trouble-free.

To test the duration of the shortest time interval for which satisfactory potential measurements can be made, the e.m.f. across a combination of a standard cell and a non-inductive resistance, through

TABLE I

Position of Rotary Switch.	Interrupter Resistance in ohms.	Time of Interruption in Seconds.		
		Current in amp.		
		10^{-1} .	10^{-2} .	10^{-3} .
1	Variable	—	—	—
2	26.9	2×10^{-5}	1×10^{-5}	1×10^{-5}
3	51.8	3	2	2
4	91.8	6	4	5
5	212	14	10	11
6	303	20	15	16
7	459	30	23	25
8	1060	70	52	56
9	1840	12×10^{-4}	9×10^{-4}	10×10^{-4}
10	2520	17	12	13
11	4590	31	23	25
12	9260	62	46	50
13	17200	11×10^{-3}	8×10^{-3}	9×10^{-3}
14	22700	15	11	12
15	47600	32	24	26
16	90900	60	45	49
17	250000	16×10^{-2}	12×10^{-2}	13×10^{-2}

which current from the interrupter was flowing, was measured. Down to a time of interruption of 5×10^{-5} sec. the minimum voltage was found as expected to be the same as that of the standard cell, independent of the voltage drop across the resistance. For yet shorter times, some small residuum of the ohmic voltage drop appeared in the minimum voltage measurement, possibly owing to inherent capacity in the circuit. Hence 5×10^{-5} sec. (position 4 on the rotary switch) was adopted as the safe lower limit of working in the electrolytic study.

General Experimental Procedure.—Experiments were carried out with a wide variety of cathodes using polarising C.D.'s of 10^{-3} to 1 amp./sq. cm. in the cell described in Part I.⁶ Except where otherwise stated a N.-HCl electrolyte at 16° was employed and the area of each electrode was 0.1 sq. cm. In general, each electrode was polarised with hydrogen passing through the electrolyte until the overvoltage had become steady, and then, after the hydrogen stream had been stopped in order to avoid influencing the rate of decay by stirring, the potentials were measured at

each setting (4-17) of the interrupter period control. At the longer time intervals, the interrupter thyatron was adjusted to flash over about once every second, as was shown by the flickering of the pointer of the polarising current meter; for the shorter times, the ratio of the on- to the off-period of the current was so great that there was no appreciable flickering of the pointer, and even at the longest period of interruption the ratio was still large. When each set of measurements had been made, the decay curve was redetermined after a further period of polarisation, and in general the potentials were found to be within 1-2 centivolts of the original values. For the measurement of the cathode potential after longer times than those given by the interrupter, the thyatron potentiometer was set to a definite voltage, and the polarising current was stopped by disconnecting the anode lead to the cell; at the same time a stop-clock was set going, and the time taken for the overvoltage to decay to the set value (as indicated by the sudden ticking of the potentiometer thyatron) was measured.

Results.

The following cathode materials have been studied: in the form of solid rods or wires—Pt, Au, Cu, Pb, Ag, Al, W, Fe, Sn, Ni; as thin films produced by electrodeposition (on copper except where otherwise stated)—platinised Pt (on platinum), Au, Cu, Ag, Ni, Rh, Bi, and Hg (formed by direct amalgamation). Where an electrode has been used in both the solid and electrodeposited forms, the latter is indicated by an asterisk.

Reproducibility of Earlier Overvoltage Results.—In view of the generally accepted opinion as to the difficulty of reproducing overvoltage values, advantage was taken of the present study to ascertain how far the results obtained a year previously and recorded in Part I⁶ could be repeated using new electrodes and with the rebuilt circuit. It was found that with the Hg, W, and platinised Pt electrodes the reproducibility was excellent; the overvoltage varied with C.D. exactly as before and the absolute values were within 2 centivolts of the previously recorded results. With the Sn, Pb, Pt, Au, Rh, and Bi electrodes the reproducibility was also very satisfactory, the shapes of the $\eta - \log I$ graphs being as before and the absolute overvoltage values being within about 5 centivolts of the earlier results; with the new solid Au electrode satisfactory overvoltage values, in reasonable agreement with those for plated Au, were obtained, whereas previously the overvoltage at solid Au had shown a very erratic behaviour with time and satisfactory measurements could not be made. In the present study, overvoltage values for both solid and plated Ni have been found to agree well with each other, and the results at the lower C.D.'s are in fair agreement with those obtained originally, but at the highest C.D. the $\eta - \log I$ graph shows a very pronounced bending-over whereas formerly a straight line was obtained. With the Al electrode the observations in general were similar to those previously made, but, owing probably to dissolution of the cathode in the acid electrolyte, anomalous values were observed at the lowest C.D. With Cu and Ag electrodes, while the variation with C.D. was similar to that originally observed, the actual values of the overvoltages were considerably lower; it is to be noted, however, that in the present experiments plated Ag as well as solid Ag has been used and the results are in satisfactory agreement with one another. The behaviour of the Fe electrode revealed a number of peculiarities. With electrodes made from different sections of the coil of wire that was used in the first investigation, a wide variety of results was obtained. In some instances the values originally recorded were precisely reproducible, while in others the absolute values of overvoltage were not only different but the $\eta - \log I$ graph was markedly curved instead of its being a straight line. The

variation in behaviour seemed to be connected with the state of the iron surface (e.g., roughness), but in spite of numerous experiments the exact conditions for the manifestation of either behaviour could not be established.

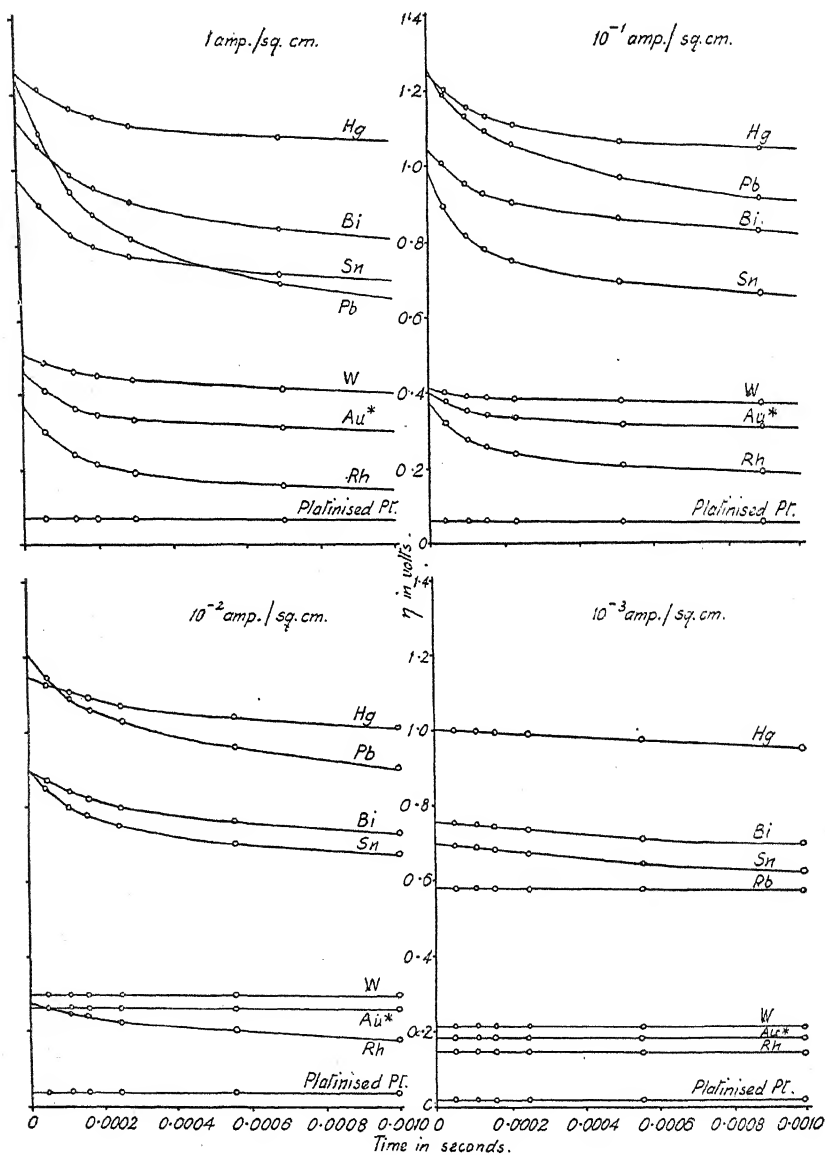


FIG. 3.—Overvoltage decay in the first thousandth second.

Notwithstanding the deviations described above, the reproducibility of the original overvoltage results is in general highly satisfactory and it affords considerable justification of the experimental method originally adopted.

The Decay of Overvoltage.—It is impossible to summarise in either tabular or graphical form all the very numerous experimental data obtained, but the general tendencies, which were very clearly marked, may be illustrated by reference to representative cases.

Decay over Short Periods.—In Fig. 3 are shown the overvoltage decay graphs over the first thousandth of a second after interruption of the current for eight electrodes that were each polarised at four different C.D.'s.

It will be seen that with the lowest polarising C.D. of 10^{-3} amp./sq. cm., the overvoltage decay over the first thousandth second is scarcely appreci-

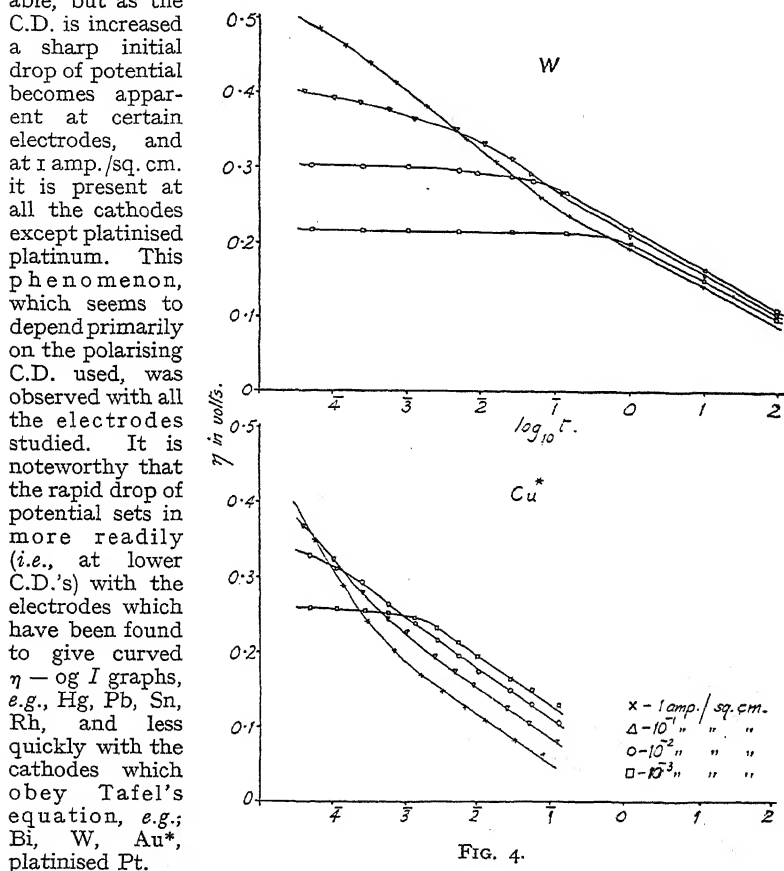


FIG. 4.

Decay over Long Periods.—The course of the overvoltage decay over long periods was studied at all the electrodes by plotting the overvoltage against the logarithm of the time. These $\eta - \log_{10} t$ graphs, while showing individual peculiarities, could all be referred to two general types illustrated by the graphs for W and Cu* in Fig. 4. In the W type, the initial overvoltage decay is dependent upon the polarising C.D. used, but after a certain time has elapsed the graphs for the different currents merge to give a straight line (within the limits of experimental error), and the linear dependence of η upon $\log t$ is then maintained down to the region of the static potential for the electrode. With the Cu* type, essentially similar phenomena are shown, but the graphs for the different currents

intersect (*vide infra*), and the straight portions do not coincide although they are parallel to one another.

These phenomena, which were common to all the electrodes studied (features of both types were sometimes combined in one electrode), would seem to indicate that the decay of hydrogen overvoltage falls into two parts:—

- (1) An initial drop depending primarily upon the polarising C.D. used.
- (2) A slower decay, characteristic of the cathode material, in which η becomes ultimately proportional to $\log t$. In all cases the time taken for the $\eta - \log t$ graph to become straight is greater the lower the polarising C.D. used.

A feature of great interest, which was frequently observed in the decay graphs, was that in a given time a high overvoltage set up at a large polarising C.D. actually decayed to a smaller value than did a lower overvoltage produced by a smaller polarising current. This phenomenon, which is most unexpected, is very clearly shown in the graphs for Cu* in Fig. 4. An extreme case of what is probably fundamentally the same behaviour was shown by the Al cathode. This electrode, which was at-

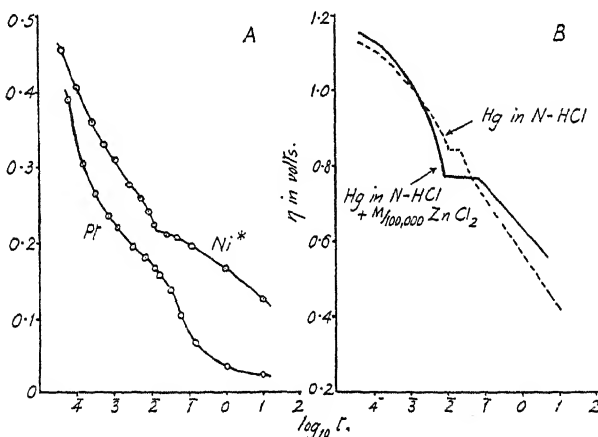


FIG. 5.

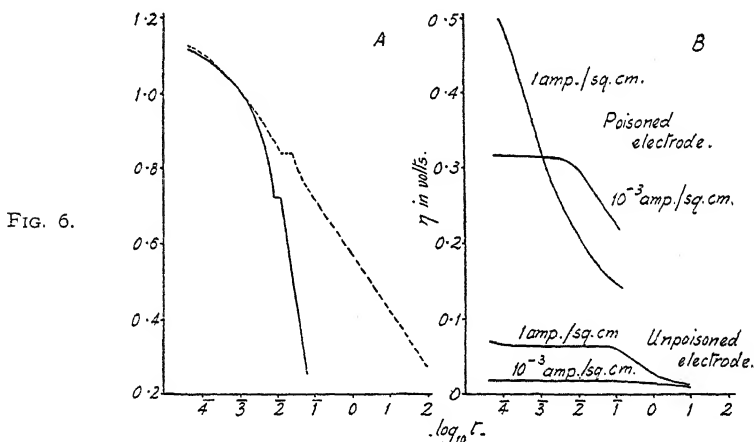
tacked somewhat by the acid electrolyte, gave a static potential with no current flowing of approximately -0.5 volt. On polarising at a high C.D., an overvoltage developed which decayed in the first hundredth of a second after the interruption of the current to a value lower than the static figure; the potential then rose towards its resting value.

These observations would seem to reinforce the conclusion arrived at above, *viz.*, that there are two largely independent processes concerned in the decay of hydrogen overvoltage, one of which becomes operative only at high C.D.'s and produces a rapid fall, while the other, which depends upon the electrode material, causes a slower decrease; it is therefore apparent that the former process may cause the overvoltage at high C.D.'s to fall to a value lower than that reached in the same time by an overvoltage set up at a low C.D. where the second process only is operative.

In further confirmation of the fact that two processes are involved in the decay of hydrogen overvoltage at high C.D.'s, it may be mentioned that the initial sections of the decay curves sometimes showed a non-uniform change of slope resulting in a sinuous graph, and with some cathodes an actual break occurred, although this may possibly be due to other causes. These phenomena are shown in Fig. 5A for Pt at 1 amp./sq. cm. and for Ni* at 10^{-1} amp./sq. cm.

With the Hg, Sn, and Bi electrodes flat portions in the decay curves extending from about 0.01 to 0.03 second were sometimes observed; with Hg this occurred at a potential of approximately -0.85 volt, and with Sn and Bi at about -0.5 volt. Similar observations were made by Bowden³ who attributed such constancies to small amounts of metallic impurities on the cathode which set up their own characteristic potentials while going into solution, and it seems likely that this was the cause in the present experiments since on the addition of a small amount of zinc chloride to the electrolyte (zinc being a not improbable impurity), the flat portion of the curve for Hg was greatly prolonged. This is shown in Fig. 5B for a Hg electrode polarised at 10^{-2} amp./sq. cm. in N. HCl, and for the same electrode after the solution had been made M./100,000 with respect to zinc chloride.

Influence of Oxygen.—To determine the effect of oxygen upon the decay of hydrogen overvoltage, experiments were carried out with a Hg electrode in N. HCl saturated with oxygen, using a calomel reference electrode. The results, which were similar at all C.D.'s, are illustrated in Fig. 6A for a polarising C.D. of 10^{-2} amp./sq. cm.; the dotted line is



the decay graph for the electrode in the oxygen-free solution. It may be noted that over the first thousandth of a second the two graphs are almost identical, but for longer times the decay in the oxygen saturated solution is very much more rapid than that normally observed. This result is to be expected in view of the work described in Part III.⁶ Once the diffusion layer has been set up with the polarising current flowing, the solution in the immediate vicinity of the cathode will be free from depolariser even in the oxygen saturated solution. On interrupting the current a certain time must elapse before oxygen can diffuse in from the body of the solution and react with the hydrogen at the cathode; after this has occurred a rapid fall of cathode potential is to be expected. It is apparent in view of this result that the initial rapid drop of overvoltage at high C.D.'s can in no way be due to the action of oxygen.

Influence of Electrode Area.—To ascertain the influence of electrode area, the decay curves for Hg were obtained in the usual electrolyte using cathodes of 0.01, 0.1, 1, and 10 sq. cm. area with a constant polarising C.D. of 10^{-2} amp./sq. cm. For all but the smallest electrode the decay graphs were identical within the limits of experimental error. With the 0.01 sq. cm. cathode, the decay followed the usual course over the first 0.003 second, and then became much more rapid than with the larger

electrodes. It seems probable that this is due merely to the inevitable loss of active material from the cathode by diffusion or reaction with traces of oxygen, which effect will be relatively much greater with the smallest electrode, and it would thus appear that electrode area is without fundamental influence on hydrogen overvoltage decay.

Influence of Catalytic Poisons.—Experiments were carried out with platinised Pt and W cathodes in *N.* HCl containing catalytic poisons such as As_2O_3 , CS_2 , and HgCl_2 which, as shown in Part IV⁶, have marked effects upon hydrogen overvoltage. The general effect of the poisons, which was very pronounced, is illustrated in Fig. 6B by the decay graphs for platinised Pt in *N.* HCl and in the same electrolyte made *M./1000* with respect to mercuric chloride, polarising C.D.'s of 1 and 10^{-3} amp./sq. cm. being used in both cases. It will be noted that with the unpoisoned electrode the decay over the first 0.1 second is very small at either C.D., but with the poisoned cathode, while the initial decay at 10^{-3} amp./sq. cm. is again slight, at 1 amp./sq. cm. a very rapid fall of overvoltage occurs over the first 0.01 second. Thus not only does the poison raise the overvoltage and change its behaviour with C.D.,¹¹ but it also causes the manifestation of the rapid initial fall of overvoltage at high C.D.'s which has been observed with other electrodes and particularly with those giving curved $\eta - \log I$ graphs (*vide supra*). Essentially similar results were observed with other poisons and with the poisoned W electrode.

Influence of Concentration and Nature of Electrolyte.—To find the effect of varying the concentration and nature of the acid electrolyte, the decay at Hg, W, and platinised Pt electrodes in *N.*, 0.1 *N.*, and 6*N.* HCl, and in *N.* H_2SO_4 and *N.* H_3PO_4 solutions was observed. In general, except under conditions such that concentration polarisation developed at the cathode,¹¹ *i.e.*, with 0.1 *N.* HCl and *N.* H_3PO_4 electrolytes at a polarising C.D. of 1 amp./sq. cm., no appreciable change in the decay graphs was observable. When concentration polarisation occurs, the fall of potential due to its disappearance on interruption of the current is superimposed upon the ordinary overvoltage decay and the graph in the initial stages is therefore very complex, but for periods greater than about 0.1 second it becomes identical with the one usually obtained. It would thus appear that, apart from this incidental effect, the concentration and nature of the acid electrolyte have little influence upon the course of the decay of hydrogen overvoltage.

Discussion.

The present study would seem to lead to a number of definite conclusions which may be briefly summarised:

(a) Two distinct processes are involved in the decay of hydrogen overvoltage at a polarised electrode.

(b) One process, which only becomes operative at C.D.'s greater than 10^{-3} amp./sq. cm., leads to a rapid drop of potential in the first thousandth of a second after interruption of the polarising current. At a C.D. of 1 amp./sq. cm. the phenomenon is shown by all the electrodes studied, except platinised platinum, and even with this cathode the process occurs if the electrode is poisoned. This rapid drop of potential takes place at lower C.D.'s with the electrodes which give curved $\eta - \log I$ graphs than with those which obey Tafel's equation, and it seems not improbable that the deviations from the equation are intimately connected with the onset of some new depolarisation process to which this rapid decay corresponds.

The present observations are in close agreement with those of Ferguson and co-workers.⁵

¹¹ Cf. Part IV⁶.

(c) At all C.D.'s there exists a second process, resulting in a slower decay of overvoltage, which follows a course such that, after a time which is greater the lower the polarising C.D., η becomes proportional to $\log t$. When this state is reached the rate of decay is independent of the polarising current used and depends solely upon the nature of the electrode material.

This view is in agreement with the conclusions reached by Baars¹ from a study of the decay of hydrogen overvoltage at low polarising C.D.'s. He suggested that the rate of this decay for any electrode, as measured by $d\eta/d \log_{10} t$, was equal to the value of b in Tafel's equation, although his own figures did not show complete correlation. Calculation of significant values of the rate $d\eta/d \log_{10} t$ from observations made in the present work was not possible in all cases, since with some electrodes the potential had dropped too near to the static value by the time the graphs for the different currents had either merged or become parallel, but the following results were obtained :

Hg 0.15	Bi 0.12	Cu* 0.06	Cu 0.05	W 0.06	Ag 0.06
Au* 0.06	Ni* 0.05	Ni 0.04	Rh 0.02		

There is no obvious relation between these figures and the values of b for the cathodes.¹²

(d) The two processes of overvoltage decay seem to be quite distinct and to proceed independently of one another. This is particularly well shown by the striking observation that in a given time a high overvoltage set up at a large C.D. may actually decay to a smaller value than a lower overvoltage produced by a small polarising current.

The theory of the decay of hydrogen overvoltage has been discussed by Butler and Armstrong² from the standpoint of the slow discharge of the hydrogen ion, and by Baars¹ on the view that overvoltage is due to an accumulation of atomic hydrogen at the electrode. The former

workers, utilising Gurney's treatment,¹³ deduce that $e^{a\eta} - e^{a\eta_0} = \frac{ka}{B} \cdot t$, where η_0 is the initial overvoltage, η is its value after time t , B is the capacity of the double layer, and a and k are constants. For all but the shortest times, this reduces to $a\eta = \log_e \frac{ka}{B} + \log_e t$, and hence,

according to these workers, the plot of η against $\log_{10} t$ should be a straight line of slope $2.303/a$, which is equal to 0.12 at ordinary temperatures. This theory is manifestly not in agreement with the experimental facts recorded in this paper. It does not contain any term which would predict the marked dependence of decay upon polarising C.D. at high currents, and while it is true that the $\eta - \log_{10} t$ graph ultimately becomes linear, its slope varies from metal to metal and is not in general 0.12. Baars assumed that the potential of a polarised electrode was proportional to the logarithm of the concentration of atomic hydrogen on the surface, and that the rate of combination of hydrogen atoms to give molecules was proportional to the square of the surface concentration; he was enabled thereby to deduce that

$$\eta = \eta_0 + \frac{RT}{F} \log_e \left(k t e^{\frac{-\eta_0 F}{RT}} + 1 \right)$$

¹² Cf. Part I⁵.

¹³ *Proc. Roy. Soc., A*, 1931, 134, 137.

where R , T , and F have their usual significance and k is a constant for the electrode. When the left-hand term in the bracket is much greater than unity, as it is after the overvoltage has decayed for some time and

t is large, this reduces to $\eta = \frac{RT}{F} \log_e k + \frac{RT}{F} \log_e t$. Although this

expression gives the necessary logarithmic relation between η and t , it is open to the criticisms that have been made of Butler and Armstrong's expression, and it suggests that the rate of decay $d\eta/d \log_{10} t$ has a universal value of 0.058 at room temperature. Since this latter point was not in agreement with the experimental facts known to him, and other difficulties inherent in the simple atomic hydrogen theory of overvoltage had to be overcome, Baars alternatively suggested that the potential of the polarised cathode might be a linear function of the surface concentration of atomic hydrogen, and that the loss of hydrogen atoms from the surface might be an exponential function of their concentration. Adopting these postulates, he deduced that the course of the decay would then be represented by the equation

$$\eta = A - \frac{B}{k_2} \log_e \left(k_1 k_2 t + e^{\frac{-k_2(\eta_0 - A)}{B}} \right) \text{ where } A, B, k_1, \text{ and } k_2 \text{ are constants.}$$

This equation reduces to the ordinary logarithmic relation for appreciable values of t , and, what is to some extent in agreement with experiment, it does this more quickly the higher the initial overvoltage, but the slopes of the $\eta - \log_{10} t$ graphs, while now dependent upon the electrode material, would have values numerically equal to those of b in Tafel's equation, and this is not so for the present results. Furthermore, the treatment does not predict the rapid fall of potential at high C.D.'s which is so significant a feature of the present study.

It must therefore be concluded that none of the overvoltage theories so far advanced is adequate for the explanation of the experimental observations on the decay of hydrogen overvoltage.

Summary.

1. The decay of hydrogen overvoltage upon interruption of the polarising current has been studied at eighteen electrodes by a new method which permits of observation of the process from a minimum time of 5×10^{-6} second.

2. Two distinct processes are involved in the decay. One, which becomes operative only at C.D.'s greater than 10^{-3} amp./sq. cm., leads to a rapid drop of potential in the first thousandth of a second, and depends primarily upon the polarising C.D. used; this process occurs at lower C.D.'s with the electrodes which show deviations from Tafel's equation, but is common to practically all the electrodes at a sufficiently high C.D. At all C.D.'s there exists a second process, resulting in a slower decay of overvoltage, which follows a course such that, after a time which is greater the lower the polarising C.D., the overvoltage becomes proportional to the logarithm of the time; when this state is reached, the rate of decay depends solely upon the nature of the electrode material.

3. The discussion of these results in the light of current theories of overvoltage is considered, and it is concluded that these views are inadequate for the description of the phenomena observed.

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University College, Leicester.

THE PHOTOCHEMICAL PRIMARY PROCESS OF IONS IN AQUEOUS SOLUTIONS.

By JOSEPH WEISS.

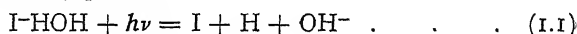
Received 5th June, 1941.

The photochemical primary process of negative ions in aqueous solutions, corresponding to their absorption in the ultraviolet, was first investigated by Franck and Scheibe¹ in the case of the halogen ions. They interpreted the primary as an electron affinity spectrum according to: $X^- + h\nu = X + \text{electron}$ (X^- halogen ion). By this theory several important features of the photochemical behaviour of these ions could be explained. In 1931 Franck and Haber² established a more complete theory which provides a full understanding of the photochemistry of negative ions. This theory was confirmed by experimental work on the halogen ions³ on sulphites and arsenites^{4, 5} and subsequently on sulphides, hydrosulphides and simple mercaptans in alkaline solutions.⁶ More recently the photochemistry of simple positive ions was investigated by Weiss and collaborators. They showed that on irradiating with ultraviolet light a solution containing ferrous ions⁷ hydrogen gas was given off and that on the other hand ceric ions could decompose water photochemically⁸ yielding molecular oxygen. It will be shown in the following that all the experimental facts can be fully understood on the basis of the Franck-Haber theory and that no modification of this theory is necessary to explain the more recent experimental results.⁹

1. Negative Ions.

(a) Iodide Ion.

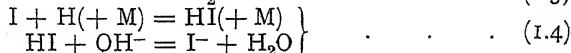
Photochemical primary process :



followed by :



reverse process :



The photochemical reaction of alkali iodides has been studied by Butkow³ who observed the formation of I_2 , which is formed with a very small quantum yield (in the absence of molecular oxygen). This is due to various types of "reverse processes," such as reactions (1.4)

¹ Franck and Scheibe, *Z. physik. Chem.*, A, 1928, **139**, 22.

² Franck and Haber, *Sitz. Preuss. Akad. Wiss.*, 1931, 250.

³ Butkow, *Z. Physik*, 1930, **62**, 71.

⁴ Haber and Wansborough-Jones, *Z. physik. Chem.*, B, 1932, **18**, 103.

⁵ Goldfinger and Albu, *ibid.*, **16**, 338.

⁶ Fishgold and Weiss, *Nature*, 1936, **137**, 71.

⁷ Weiss, *ibid.*, 1935, **136**, 794. Potterill, Walker and Weiss, *Proc. Roy. Soc. A.*, 1936, **156**, 561.

⁸ Porret and Weiss, *Nature*, 1937, **139**, 1019.

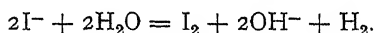
⁹ Farkas and Farkas, *Trans. Faraday Soc.*, 1938, **34**, 1113.

which in solution will be further enhanced through primary recombination.¹⁰

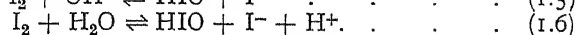
The photochemical primary process is always represented by reaction (I.1), independent of the cation present. This view is supported by the measurements of Scheibe¹¹ and Lederle¹² who found that the absorption spectrum of I^- is independent of the metal cation present for iodide concentrations 10^{-4} molar to 1 molar, and by the work of Butkow³ who observed that the photochemical liberation of iodine is about the same for CsI, KI and NaI solutions. However, Farkas and Farkas¹³ found that the photochemical formation of hydrogen gas is greater from acidified solutions than from neutral solutions. This is in agreement with the fact that the photochemical liberation of iodine from iodide solutions (in the presence of oxygen) is favoured by acid solution and probably also in solutions of lithium iodide but decreases roughly in the order: $HI > LiI > NaI > KI$.¹⁴

The interesting physical explanation put forward by Farkas and Farkas,⁹ assuming the neutralisation of the corresponding cation in the primary process (formation of a metal atom), is not in agreement with the experiments, because the primary process has been shown to be independent of the cation. In the case of acid iodide solutions it is possible that some undissociated HI molecules are present which could be split directly into the elements. This explanation has actually been put forward by Warburg and Rump¹⁵ to explain their results on aqueous HI solutions of higher concentrations where the electrolytic dissociation is probably not complete.

The case of dilute solutions containing hydrogen ions can be explained chemically through some "reverse processes" in which the primarily formed H atoms and I_2 are involved and which in any case must be taken into account. Whenever photolysis takes place in an iodide solution hydroxyl ions are formed according to the net process:



If the solution were acid originally these OH^- will be neutralised immediately. If, on the other hand, we start with a neutral solution of an iodide, the solution gradually gets more and more alkaline and the iodine present disappears through the very rapid reaction with OH^- or H_2O according to:



Both these equilibria are established very rapidly and are in alkaline solutions well on the side of IOH and I^- $\left(\frac{[I_2][OH^-]}{[I^-][IOH]} = 1.7 \times 10^{-2} (25^\circ) \right)$.

The IOH formed through the reactions (1.5 or 1.6) reacts further to give iodate¹⁶. It is quite clear that any IOH, HIO_3 or IO_3 present in the solution will act as powerful acceptor for the hydrogen atoms. The

¹⁰ Franck and Rabinovitch, *Trans. Faraday Soc.*, 1933, **29**, 120.

¹¹ Scheibe, *Z. Elektrochem.*, 1928, **34**, 497.

¹² Lederle, *Z. physik. Chem., B*, 1930, **10**, 121.

¹³ Farkas and Farkas, *Trans. Faraday Soc.*, 1938, **34**, 1120.

¹⁴ Schneider, *Z. physik. Chem., B*, 1935, **28**, 311.

¹⁵ Warburg and Rump, *Z. Physik*, 1928, **47**, 305.

¹⁶ Skrabal, *Monatsh. Chem.*, 1911, **32**, 815. Abel, *Z. physik. Chem.*, 1928, **136**, 497.

result is that the quantum yield for the formation of iodine and hydrogen is further decreased.

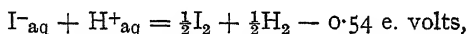
Since, thus, the primary process is not influenced by the cations present, we can now turn to the consideration of the energy changes involved in the process (I.1). The light quantum absorbed in the case of iodide ions $(h\nu)_I$ is given by :

$$\begin{aligned} (h\nu)_I &= -E_I - D_{H_2O} + E_{OH} + X \\ X &= (-H_I + H'_{OH}) \end{aligned}$$

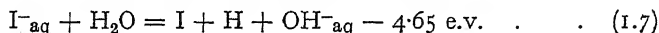
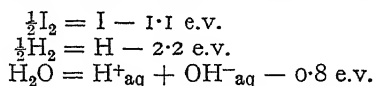
where E_I is the electron affinity of I atom, D_{H_2O} the dissociation energy of water into H and OH, E_{OH} the electron affinity of OH radical, and X' the difference of potential energy of the electron in the initial and final position. This difference is mainly due to the hydration energy of the iodide ion (H_I) being different from that of the OH^- ion which is formed in the reaction. However, according to the Franck-Condon principle the full hydration energy of the hydroxyl ion formed in the reaction cannot be attained because the "heavy" dipoles cannot follow completely the electron jump. In agreement with Farkas and Farkas⁹ we shall denote this incomplete hydration energy by H'_{OH} . Farkas and Farkas have introduced the term "electron affinity of the water molecule" for the expression $(E_{OH} + H'_{OH} - D_{H_2O})$. The primary step most probably consists of an attachment of the photo-electron to one of the water molecules in the hydration shell,⁷ and therefore this notation seems quite justified.

However, the introduction of these new terms does not alter the actual energy requirement for the primary process.

The energy necessary for the formation of H and I atoms from iodide solutions can be calculated independently from the electrochemical normal potential of the I_2/I^- electrode, the value of which is + 0.54 volt measured against the hydrogen electrode¹⁷ at 25° C. This corresponds to the reaction : *



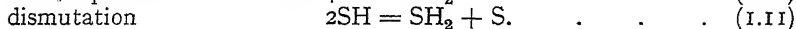
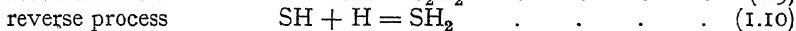
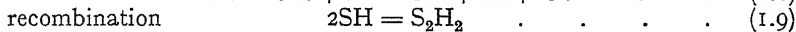
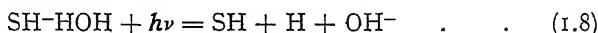
combined with :



According to Butkow⁸ no decomposition takes place above a wave length of $\lambda \sim 2570 \text{ \AA}$. This corresponds to an energy of about 4.8 e.v.

(b) Hydrosulphide and Mercaptan Ions.

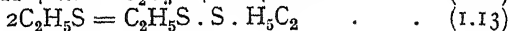
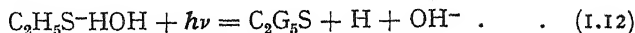
Photochemical primary process :



* Here and in the following thermochemical equations the subscript "aq" denotes the fully hydrated ions. In some cases the total energies (heats of formation) have been used instead of the free energies. However, at room temperature this difference never exceeds $\pm 0.5 \text{ e.v.}$

¹⁷ Gurney, *Ions in Solution* (Cambridge, 1936).

Similarly in the case of simple mercaptans (*e.g.*, ethyl mercaptan) in alkaline solution :



The formation of disulphides and molecular hydrogen and sulphur, formed according to the above reactions has been observed experimentally by Weiss and Fishgold.⁶ They are formed with a low quantum yield. This is due to the reverse processes (1.10 and 1.14) and in particular to the dismutation process in the case of SH (reaction 1.11).

According to a recent theoretical discussion¹⁸ the dismutation processes assume great importance in the case of radicals with a large dipole moment (*e.g.*, SH) because the coulombic repulsion interferes with the recombination process.

The light quantum needed for the photochemical decomposition of hydrosulphide according to reaction 1.8 is given by the equation :

$$\begin{aligned} - (h\nu)_{\text{SH}} &= -E_{\text{SH}} - D_{\text{H}_2\text{O}} + E_{\text{OH}} + X = -6.56 \text{ e.v.} + H'_{\text{OH}} \\ X &= -H_{\text{SH}} + H'_{\text{OH}} \\ H'_{\text{OH}} &= 6.56 \text{ e.v.} - (h\nu)_{\text{SH}} = 2.06 \text{ e.v.} \end{aligned}$$

where E_{SH} is the electron affinity of SH radical = 2.65 e.v.,¹⁹ $D_{\text{H}_2\text{O}}$ the dissociation energy (into H and OH) = 5.0 e.v., E_{OH} the electron affinity of OH radical = 3.7 e.v.,²⁰ and H_{SH} the hydration energy of SH^- ion = 2.61 e.v.¹⁹

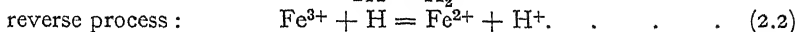
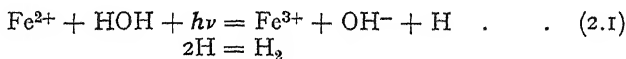
The wave-lengths necessary to decompose SH^- ions in solution was found to be $\lambda \sim 2700 \text{ \AA}$.^{6, 21} This corresponds to an energy $(h\nu)_{\text{SH}} \sim 4.5$ e.v. and leads to the value of $H'_{\text{OH}} \sim 2.06$ e.v. The full hydration energy of OH^- ions is 3.8 e.v.²² so that 54 per cent. of it is utilised in the above process.

2. Positive Ions.

(a) Ferrous Ion.

On irradiation in the ultraviolet, hydrogen gas is evolved and an equivalent amount of ferric ions formed :

photochemical primary process :



The low quantum yield which is practically independent of the hydrogen ion concentration⁷ is due to the reverse process (2.2). This is further illustrated by the fact that in solutions which contain even a very small amount of ferric ions at the beginning no evolution of hydrogen takes

¹⁸ Weiss, *Trans. Faraday Soc.*, 1935, **31**, 966.

¹⁹ West, *J. Physic. Chem.*, 1935, **39**, 493.

²⁰ Weiss, *Trans. Faraday Soc.*, 1940, **36**, 856.

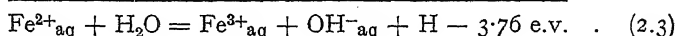
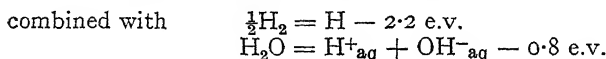
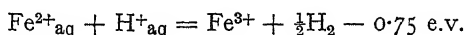
²¹ Ley and Arends, *Z. physik. Chem.*, B, 1931, **15**, 311.

²² Van Arkel and de Boer, *Die chemische Bindung als elektrostatische Erscheinung* (Hirzel, 1931).

place at all. The energy necessary for the primary process according to reaction (2.1) is given by :

$$\begin{aligned}(h\nu)_{\text{Fe}} &= -I_{\text{Fe}^{3+}} - D_{\text{H}_2\text{O}} + E_{\text{OH}} + X \\ X &= (-H_{\text{Fe}^{3+}} + H_{\text{OH}} + H_{\text{Fe}^{3+}}).\end{aligned}$$

This energy can also be calculated from the $\text{Fe}^{3+}/\text{Fe}^{2+}$ electrochemical potential, the value of which is +0.75 volts¹⁷ measured against the hydrogen electrode (at 25°). This corresponds to the reaction :



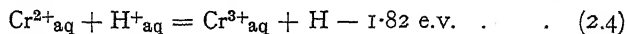
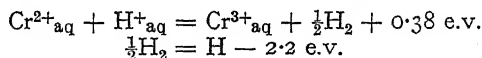
The photochemical decomposition requires 4.5 e.v.⁷ The difference of 0.8 e.v. must be attributed to the incomplete hydration of the OH^{-} and Fe^{3+} formed in the reaction.

Farkas and Farkas⁴ have correctly deduced the energy requirement of 4.5 e.v. for the reaction ($\text{Fe}^{2+}_{\text{aq}} = \text{Fe}^{3+}_{\text{aq}} + \text{electron}$). However, they assume that this reaction represents the actual photochemical process which takes place on irradiation, because they compare this value of 4.5 e.v. with the experimentally observed one. This is, of course, not the case; the actual photochemical process which takes place is represented by reaction (2.3), which only requires 3.76 e.v. and there is an excess energy of 0.74 e.v. available to balance the incomplete hydration.

It is of interest to compare with this the energy changes involved in the thermal evolution of hydrogen which takes place in the acid solutions of chromous and titanous ions. Both these reactions are accelerated in the presence of platinised platinum.

(b) Chromous and Titanous Ions.

The $\text{Cr}^{3+}/\text{Cr}^{2+}$ normal potential, measured against the hydrogen electrode is -0.38 e.v. (25° C.) therefore we have the reactions :



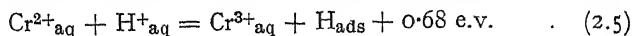
This reaction is fairly endothermic and it is doubtful whether it can take place at all in homogenous solution. It is not impossible that it proceeds, even under ordinary conditions as a wall reaction.

In the presence of platinised platinum the reaction is greatly accelerated. The reason for this may be found in the fact that the hydrogen atoms formed in reaction (2.4) are not formed free in solution but are adsorbed on the surface of the platinum. We thereby gain the adsorption energy given by :²³

$$\text{H} = (\text{H})_{\text{ads}} + 2.5 \text{ e.v.}$$

²³ Lennard-Jones, *Trans. Faraday Soc.*, 1932, 28, 341.

and obtain for the reaction in the presence of the heterogenous catalyst :



followed by the recombination of the adsorbed hydrogen atoms to give H_2 .

Similar considerations hold for the case of thermal evolution of hydrogen from acid solutions containing Ti^{3+} ions.

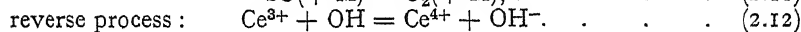
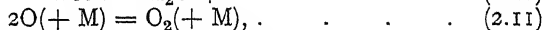
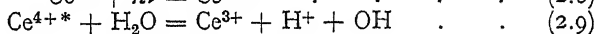
(c) Ceric Ion.

The photochemical behaviour of Fe^{2+} ion is in a way similar to that of negative ions. In both cases the primary process corresponds to an electron affinity spectrum: the electron is detached under the influence of a light quantum and decomposes the water.

The photochemical behaviour of ceric ion belongs to a different category.

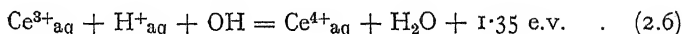
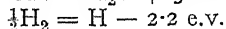
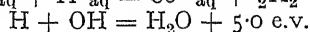
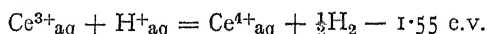
The ceric ion is first raised to an excited state by the light absorption and the excited ceric ion (Ce^{4+*}) is then capable of extracting an electron from one of the water molecules in its hydration shell, which is thereby oxidised finally yielding molecular oxygen and hydrogen ions.

Photochemical primary process :



It may be that it is not permissible to separate the reaction (2.8 and 2.9) and that they both occur in one act. The formation of excited ceric ions of any lifetime depends on whether or not ceric ions in solution show any marked fluorescence (corresponding to the reverse process ($\text{Ce}^{4+*} \rightarrow \text{Ce}^{4+} + h\nu$)). However, it is not to be expected that aqueous ceric salt solutions show fluorescence, because H_2O molecules are very efficient in quenching this fluorescence by reacting with the excited ion according to reaction (2.9) before it has time to emit fluorescence.

The energy for the net process can be again calculated from the known electrochemical potential $\text{Ce}^{4+}/\text{Ce}^{3+}$ which is $+1.55$ volts¹⁷ (against the hydrogen-electrode, at 25°).

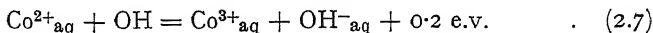
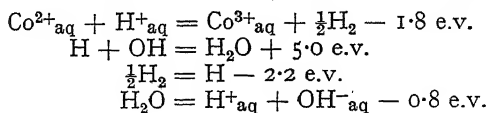


The absorption spectrum of ceric ions in solution has been determined by Porret and Weiss.⁸ The long wave absorption limit was found at $\lambda \sim 5100 \text{ \AA}$, corresponding to an energy of 2.4 e.v. ; the difference of about 1 e.v. arising again out of the incomplete hydration during the electron jump.

A similar calculation can be carried out for the thermal formation of O_2 by cobaltic ions which was studied by Foerster and Oberer.²⁴ The experimental data lend support to the view that the cobaltic ions interact

²⁴ Oberer, *Dissertation*, Zurich, 1903.

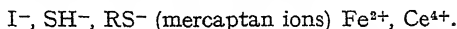
with OH^- ions directly because the velocity of the reaction decreases with increasing H^+ concentration. The normal potential of the $\text{Co}^{3+}/\text{Co}^{2+}$ is +1.8 volts¹⁷ (against the hydrogen-electrode, at 25°).



Ceric ions require at least 1.35 e.v. in order to decompose water into H^+ ions and OH radicals, whereas cobaltic ions can discharge hydroxyl ions in a reaction which is endothermic with only 0.2 e.v., and, therefore, can go on even at room temperature.

Summary.

1. More recent experimental work on the photochemical primary process of the following ions has been discussed :



2. The photochemical primary processes are adequately described by the theory of Franck and Haber but a number of chemical factors have to be taken into account for the secondary reactions. For instance, in the case of iodide ions the reaction of iodine molecules with OH^- or H_2O is capable of explaining the different behaviour of acidified solutions.

3. The energy necessary for the photochemical decompositions have been calculated independently from the corresponding electrochemical oxidation-reduction potentials (ferrous/ferric, cerous/ceric etc.).

4. The thermal formation of hydrogen gas from chromous solutions and the thermal formation of molecular oxygen from cobaltic solutions are discussed from a similar point of view.

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THE FORCE CONSTANTS OF SOME CARBON-CARBON BONDS.

By J. W. LINNETT.

Received, 25th April, 1941.

In a recent paper Crawford and Brinkley¹ have considered the application of a normal co-ordinate treatment to the related molecules hydrogen cyanide, acetylene, ethane, dimethyl-acetylene, methyl-acetylene, and methyl cyanide. They find that by transferring force constants of similar links from molecule to molecule in this series it is possible to calculate the 52 fundamental frequencies of these six molecules, using only 20 distinct force constants. For the force constant of the carbon-carbon link in ethane they use 4.50×10^5 dynes per cm., the value given by Stitt.² This agrees closely with the value of 4.53×10^5 used by Linnett,³ and there seems to be no doubt that the force constant

¹ Crawford and Brinkley, *J. Chem. Physics*, 1941, 9, 69.

² Stitt, *ibid.*, 1939, 7, 297.

³ Linnett, *ibid.*, 1940, 8, 91.

of this linkage is close to 4.5×10^5 . For the force constant of the carbon-carbon linkage in methyl cyanide Crawford and Brinkley give the value 4.94×10^5 , which does not agree very well with that used by Linnett, namely 5.3×10^5 dynes per cm.

Fox and Martin⁴ showed that for the carbon-carbon link in the molecules ethane, ethylene and acetylene the values of $k \cdot r_e^5$ approximated closely to a constant value (see Table II), although the value of k , the force constant, changed by a factor of between three and four times on passing from ethane to acetylene. Since the length of the carbon-carbon bond in methyl cyanide has been determined,⁵ the Fox-Martin relation may be used to fix approximately the magnitude of the carbon-carbon force constant in this molecule. Using $k \cdot r_e^5 = 40.4 \times 10^5$, $k = 4.93 \times 10^5$ gives $r_e = 1.525$ Å, while $k = 5.3 \times 10^5$ gives $r_e = 1.50$ Å. Pauling, Springall and Palmer find, by the electron diffraction method, that $r_e = 1.49 \pm 0.03$, which supports the value of 5.3×10^5 for the force constant of the bond rather than 4.93×10^5 .

Crawford and Brinkley give for the carbon-carbon single bond force constant in methyl and dimethyl-acetylene the value 5.183×10^5 . Using $k \cdot r_e^5 = 40.4 \times 10^5$ this gives for r_e the value 1.51 Å, which does not agree at all well with the spectroscopically determined value⁶ of 1.462 Å. Because of this discrepancy it seemed of interest to consider the application to the methyl-acetylenes of a force field analogous to that used successfully by the author for ethane, the methyl halides, methyl cyanide and isocyanide.

Dimethyl-acetylene.

The frequencies used were those given by Crawford⁷ and used by Crawford and Brinkley in their calculations. The methyl group was assumed to be tetrahedral with $r_{CH} = 1.093$ Å,⁸ and the four carbon atoms linear with the lengths of the single and triple bonds 1.462 and 1.204 Å respectively. Any small alteration of these bond lengths will not alter the calculations appreciably.

The potential function used was:—

$$V = \frac{1}{2} \Sigma k_{CH} (\Delta CH)^2 + \frac{1}{2} \Sigma k_{C-C} (\Delta C-C)^2 + \frac{1}{2} k_{C \equiv C} (\Delta C \equiv C)^2 + \frac{1}{2} \Sigma k_{HCH} (\Delta HCH)^2 \\ + \frac{1}{2} \Sigma k_{HC-C} (\Delta HC-C)^2 + \frac{1}{2} \Sigma k_{CCC} (\Delta CCC)^2 + \frac{1}{2} \Sigma k' (\Delta C-C) (\Delta HCH) \\ + \frac{1}{2} k'' (\Delta CCC') (\Delta CCC'').$$

This is a simple valency force field function with two additional cross-terms. The first cross-term, representing the interaction of the carbon-carbon single bond with the angles of the methyl group, was found to be important in ethane, the methyl halides, methyl cyanide and isocyanide.⁹ The second, representing the interaction between the alteration of the adjacent angles in the straight chain of four carbon atoms, is presumed to be of importance in this molecule since the inclusion of an analogous cross-term has been found to be essential in the case of acetylene.⁹ There are six main constants and two cross-term constants.

Using the following values of the constants: $k_{CH} = 4.8 \times 10^5$; $k_{C-C} = 5.5 \times 10^5$; $k_{C \equiv C} = 15.3 \times 10^5$; $k_{HCH} = 0.534 \times 10^{-11}$ dyne cm., per radian; $k_{HC-C} = 0.686 \times 10^{-11}$; $k_{CCC} = 0.345 \times 10^{-11}$; $k' =$

⁴ Fox and Martin, *J. Chem. Soc.*, 1939, 884.

⁵ Pauling, Springall and Palmer, *J.A.C.S.*, 1939, 61, 927.

⁶ Herzberg, Patat and Verleger, *J. Physic Chem.*, 1937, 41, 123.

⁷ Crawford, *J. Chem. Physics*, 1939, 7, 555.

⁸ Barker and Ginsberg, *ibid.*, 1935, 3, 668.

⁹ Colby, *Physic. Rev.*, 1935, 47, 388.

-1.09×10^{-3} ; and $k'' = 0.311 \times 10^{-1}$, the calculated frequencies are those shown in Table I. It will be seen that the calculated frequencies agree well with those observed.

Methyl-acetylene.

The frequencies employed were those determined by Crawford¹⁰ and used by Crawford and Brinkley. The analogous distances and angles were assumed to be the same as in dimethyl-acetylene, and the acetylene carbon-hydrogen distance was taken to be 1.057 Å.

The potential function used was:

$$V = \frac{1}{2}\Sigma k_{\text{CH}}(\Delta\text{CH})^2 + \frac{1}{2}k'(\Delta\text{CH}')^2 + \frac{1}{2}k_{\text{C-C}}(\Delta\text{C-C})^2 + \frac{1}{2}k_{\text{C}\equiv\text{C}}(\Delta\text{C}\equiv\text{C})^2 \\ + \frac{1}{2}\Sigma k_{\text{HCH}}(\Delta\text{HCH})^2 + \frac{1}{2}\Sigma k_{\text{HC-C}}(\Delta\text{HC-C})^2 + \frac{1}{2}k_{\text{CCC}}(\Delta\text{CCC})^2 \\ + \frac{1}{2}k_{\text{C}\equiv\text{CH}}(\Delta\text{C}\equiv\text{CH})^2 + \frac{1}{2}\Sigma k''(\Delta\text{C-C})(\Delta\text{HCH}) + \frac{1}{2}k'''(\Delta\text{CCC})(\Delta\text{C}\equiv\text{CH}).$$

This potential function is precisely analogous to that used for dimethyl-acetylene.

Giving k_{CH} , $k_{\text{C-C}}$, $k_{\text{C}\equiv\text{C}}$, k_{HCH} , $k_{\text{HC-C}}$, k_{CCC} , and k' the same values as in dimethyl-acetylene, and taking $k'_{\text{CH}} = 6.3 \times 10^5$ dynes per cm.,

$k_{\text{C}\equiv\text{CH}} = 0.24 \times 10^{-11}$,
and $k''' = 0.30 \times 10^{-11}$,

the calculated frequencies are those shown in Table I. There is good agreement with the observed values.

TABLE I.

OBSERVED AND CALCULATED FREQUENCIES
(IN CM.⁻¹).

Symmetry Class.	Observed.	Calculated.	Percentage Error.
Dimethyl-acetylene.			
A_1	2916	2902	-0.5
	2270	2271	0
	1380	1378	-0.2
\bar{A}_2	725	708	-2.3
	2976	2894	-2.8
	1380	1387	+0.6
E	1126	1152	+2.3
	2976	3012	+1.2
	1468	1457	-0.8
\bar{E}	1050	1049	-0.1
	213	213	0
	2966	3012	+1.5
	1448	1457	+0.6
	1029	1051	+2.2
	371	371	0
Methyl-acetylene.			
A_1	3430	3439	+0.3
	2910	2893	-0.6
	2151	2146	-0.2
E	1380	1365	-1.1
	926	930	+0.4
	2995	3011	+0.5
	1444	1458	+1.0
	1041	1038	-0.3
	642	642	0
	333	333	0

and the four frequencies below 700 cm.⁻¹ are determined exactly by four constants. The reproduction of 25 frequencies by eleven constants.

¹⁰ Crawford, *J. Chem. Physics*, 1940, 8, 526.

indicates the general correctness of the force field employed; $k_{\text{C-C}}$, the constant in which we are particularly interested, is one of the four that determines the twelve frequencies between 700 and 1500 cm^{-1} . Since over these twelve frequencies the average error is only 1.0% it may be presumed that the value obtained for this constant is reliable.

Using $k \cdot r_e^5 = 40.4 \times 10^5$ and $k = 5.5 \times 10^5$ the calculated value of r_e is 1.49 Å, compared with 1.51 obtained using the value $k = 5.183 \times 10^5$ given by Crawford and Brinkley. The difference between the constants calculated here and those calculated by Crawford and Brinkley arises because different values have been taken for the important cross-term constant, called in this paper k' . Crawford and Brinkley have used in both methyl acetylenes and in methyl cyanide the value for the cross-term constant that they found to apply in ethane. Since the carbon-carbon bond has changed it would seem to be unjustifiable to use in these molecules the same value for the cross-term constant that was used in ethane. Neither of the above values for the internuclear distance obtained using the Fox-Martin relation agree with the observed spectroscopic value of 1.462 Å obtained by Herzberg, Patat and Verleger.⁶ Pauling, Springall and Palmer,⁵ using the electron diffraction method, find the length of this carbon-carbon single bond in methyl-acetylene to be 1.46 ± 0.02 , and in dimethyl-acetylene to be 1.47 ± 0.02 Å. The value 5.5×10^5 for the carbon-carbon force constant was obtained in the first place for dimethyl-acetylene, and then transferred to methyl-acetylene. The calculated $r_e = 1.49$ Å is in agreement therefore, within the limits of error, with the electron diffraction value for dimethyl-acetylene. The observed bond length makes the force constant of 5.183×10^5 ascribed by Crawford and Brinkley to this linkage extremely unlikely since it corresponds to a bond length of 1.51 Å, a value certainly outside the possible limits of error.

In Table II are given the values of the force constant k , the bond length r_e , and $k r_e^5$ for the carbon-carbon bonds in ethane, methyl cyanide, dimethyl-acetylene, ethylene and acetylene. The values of k for ethylene and acetylene are taken to be 9.8×10^5 ¹¹ and 15.8×10^5 ¹² respectively. The other values are those already recorded. In the last column are given the bond lengths calculated using $k \cdot r_e^5 = 40.4 \times 10^5$ and the force constants listed in the first column. 40.4×10^5 is the mean of the results for $k \cdot r_e^5$ obtained with ethane, ethylene and acetylene.

TABLE II.

THE FORCE CONSTANTS AND BOND LENGTHS OF SOME CARBON-CARBON LINKAGES.

Molecule.	k .	$r_e(\text{obs.})$.	$k \cdot r_e^5$.	$r_e(\text{calc.})$.
Ethane	4.5×10^5	1.55	40.25×10^5	1.551
Methyl cyanide . .	5.3×10^5	1.49	38.94×10^5	1.50
Dimethyl-acetylene .	5.5×10^5	1.47	37.75×10^5	1.49
Ethylene	9.8×10^5	1.331 ¹³	40.95×10^5	1.327
Acetylene	15.8×10^5	1.204 ¹⁴	39.97×10^5	1.206

¹¹ Thompson and Linnett, *J. Chem. Soc.*, 1937, 1376.

¹³ Thompson, *Trans. Faraday Soc.*, 1939, 35, 697.

¹⁴ Herzberg, Patat and Spinks, *Z. Physik*, 1934, 91, 386.

¹² *Ibid.*, 1384.

Conclusion.

The values given by Crawford and Brinkley for the force constants of the carbon-carbon single bonds in the methyl-acetylenes and methyl cyanide appear to be too small and more satisfactory values are 5.5 and 5.3×10^5 dynes per cm. respectively. It seems that care must be taken in the transference of force constants, particularly cross-term constants, from molecule to molecule, even among those of similar type. In the cases considered above it seems preferable to use a rather simpler potential function and then to calculate the force constants separately for each molecule. This course is supported by recent work on heats of linkages, which are related to force constants in so far as they both measure bond strengths. Kistiakowsky and his co-workers¹⁵ and Baughan and Polanyi¹⁶ have shown that the heats of formation of linkages which are apparently similar vary appreciably in an homologous series of molecules.

The length of the carbon-carbon single bond in dimethyl-acetylene appears to be in the neighbourhood of 1.47 Å, though a value rather larger than this, perhaps 1.48 or even 1.49 , is favoured by the force constant calculations.

Summary.

The twenty-five fundamental vibration frequencies of the two methyl acetylenes have been calculated, using a potential function involving eleven constants. The values obtained for the force constant of the carbon-carbon single bond in these molecules and for that in methyl cyanide are discussed, and compared with the values given by Crawford and Brinkley.

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¹⁵ See Conant and Kistiakowsky, *Chem. Rev.*, 1937, **20**, 181.

¹⁶ Baughan and Polanyi, *Nature*, 1940, **146**, 685.

A THERMODYNAMIC STUDY OF BIVALENT METAL HALIDES IN AQUEOUS SOLUTION.¹ PART II. THE ACTIVITY COEFFICIENTS OF CALCIUM, STRONTIUM AND BARIUM CHLORIDES AT 25° C. A NOTE.

By J. R. I. HEPBURN and J. E. GARSIDE.

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In this paper¹ the author makes no reference to a paper by one of the present authors² which covers the same ground, discusses in the same way the same comparative E.M.F. data, and comes to the same general conclusions.

¹ Robinson, *Trans. Faraday Soc.*, 1940, **36**, 735.

² "The vapour pressure of water over aqueous solutions of the chlorides of the alkaline earth metals. Part IV. Evaluation of activity coefficients." *J. Chem. Soc.*, 1932, 1284.

Comparison of the results of Robinson and those of Hepburn may be made by equating the values for a particular concentration, as pointed out in the earlier paper (*loc. cit.*³, p. 1288). Table I shows the comparison. The concentration figures are taken from the original paper of 1932. The values of γ for CaCl_2 are equated at a concentration of 0.494 M, for SrCl_2 at a concentration of 0.400 M, and for BaCl_2 at a concentration of 0.508 M. The figures of Robinson are in each case read off from a graph of the experimental results.

The agreement is seen to be fairly good; both sets of figures indicate that in each case the activity coefficient passes through a minimum value. Thus for CaCl_2 a minimum occurs in Robinson's figures at 0.5 M, in Hepburn's figures at 0.6 M. Similarly for SrCl_2 both sets of figures show

a minimum at 0.6 M. For BaCl_2 the figures of Robinson show a minimum at 0.8 M, those of Hepburn at 1 M.

A further point arises in connection with the method used by Robinson to deduce the vapour pressure from the standard data for solutions of KCl.

In the experimental method employed by Robinson, a given solution is allowed to reach vapour pressure equilibrium at 25° C. with a solution of KCl (employed throughout as a standard). Determinations of the concentration of each solution follow, and the concentrations of a series of such "isopiestic" solutions are recorded in the work.

The method is evidently completely relative, and its absolute accuracy is entirely dependent upon the accuracy of the vapour pressure data for KCl. These data were originally taken by Sinclair³ from the results of Lovelace, Fraser and Sease⁴ which were obtained directly at 20° C. by a tensimetric method using the Rayleigh

TABLE I.
ACTIVITY COEFFICIENTS FOR CALCIUM, STRONTIUM AND BARIUM CHLORIDES AT 25° C.

M.	Activity Coefficient, γ .		
	Hepburn.		Robinson.
CaCl_2			
0.494	0.502	(0.457)	0.457
0.635	0.498	0.453	0.464
0.796	0.517	0.471	0.479
1.000	0.528	0.481	0.509
1.504	0.671	0.611	0.627
1.985	0.884	0.805	0.801
SrCl_2			
0.400	0.427	(0.430)	0.430
0.600	0.401	0.404	0.426
0.995	0.446	0.449	0.454
1.495	0.549	0.553	0.526
2.246	0.752	0.757	0.702
BaCl_2			
0.508	0.394	(0.390)	0.390
0.606	0.376	0.372	0.386
1.007	0.348	0.344	0.392
1.285	0.352	0.348	0.408
1.568	0.408	0.404	0.429
1.655	0.414	0.410	0.437
1.788	0.418	0.414	0.447

manometer, and appear to be regarded as among the most accurate absolute vapour pressure data on record. Later, in a paper by Robinson and Sinclair⁵ the standard vapour pressure data for KCl solutions were "corrected" at concentrations between 0.1 and 1 M by bringing into consideration figures calculated from results obtained by E.M.F. measurements. This procedure appears to have been adopted because of the necessity for smoothing out what was described as a "kink" in the plot of p/p_0 against M, using the data of Lovelace, Fraser and Sease. It may be added that in the opinion of these latter authors the irregularities were regarded as being entirely too great to be attributed to experimental error, the points on the curve having been determined with great care (*loc. cit.*⁴, p. 106).

³ J. Physic. Chem., 1933, 37, 495.

⁴ J. Amer. Chem. Soc., 1921, 43, 102.

⁵ *Ibid.*, 1934, 56, 1832.

Hepburn has pointed out (*loc. cit.*², p. 568) that KCl is not unique in showing anomalous behaviour over the concentration range 0.1-1 M. For example, from the results obtained in 1932, calcium, strontium and barium chlorides show a similar behaviour. It is of particular interest that the actual results of Robinson for these salts, when plotted as were those of Lovelace, Fraser and Sease (*i.e.*, p_M v. M : see Fig. 1) give a

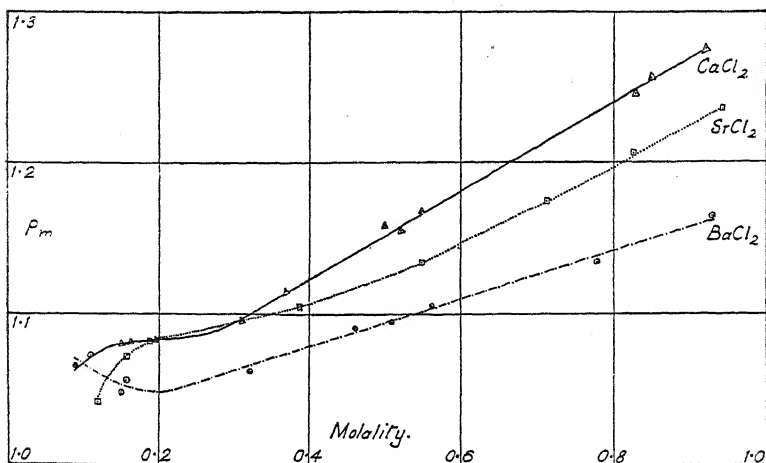


FIG. 1.

clear indication of anomalous behaviour, which, moreover, is found whether the "corrected" vapour pressure data mentioned above, or the original results of Lovelace, Fraser and Sease are used to deduce the vapour pressure.

It is also possible to provide an independent check of the "corrected" figures of Robinson and Sinclair. Robinson has recently published isopiestic data on sulphuric acid solutions⁶ from which the vapour pressure may be deduced (1) using the "corrected" figures for the standard KCl solutions or (2) using the uncorrected figures. These vapour pressure figures may then be compared with the standard data determined directly at 25° C. by Grollmann and Fraser.⁷ In Table II figures are given for the vapour pressure of KCl solutions at 25° C. recalculated by the authors

TABLE II.

VAPOUR PRESSURE LOWERING, AT 25° C., FOR AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE.

M.	$R = (p_0 - p)/Mp_0 \times 10^{-5}$		$(p_0 - p)_{25^\circ \text{C.}}$	
	Corrected.	Uncorrected.	Corrected.	Uncorrected.
0.1	3332	3275	0.079	0.078
0.2	3279	3215	0.156	0.153
0.3	3253	3194	0.232	0.228
0.5	3220	3180	0.383	0.378
1.0	3201	3173	0.760	0.754

from the data given by Robinson and Sinclair over the concentration range 0.1-1 M. The degree of divergence between the "corrected" values and those originally obtained by Lovelace, Fraser and Sease is indicated. Figures for concentrations higher than 1 M do not enter into discussion,

⁶ These Trans., 1939, 35, 1229.

⁷ J. Amer. Chem. Soc., 1925, 47, 714.

since over this range Robinson and Sinclair accept the figures of Lovelace, Fraser and Sease as standard.

Table III gives the experimental results of Grollmann and Fraser for H_2SO_4 solutions, together with the corresponding results of Robinson, as read off from a large scale plot. A comparison of the figures immediately

TABLE III.

VAPOUR PRESSURE LOWERING, AT $25^\circ C.$,
FOR AQUEOUS SOLUTIONS OF SULPHURIC
ACID.

M.	$(p_0 - p)_{25^\circ C.}$		
	Grollmann and Fraser.	Robinson.	
		Uncorrected.	Corrected.
0.195	0.163	0.164	0.167
0.221	0.184	0.185	0.188
0.350	0.293	0.294	0.300
0.483	0.411	0.412	0.417
0.583	0.499	0.503	0.509
0.638	0.549	0.550	0.556
0.710	0.613	0.619	0.626
0.749	0.651	0.656	0.664
0.791	0.692	0.698	0.706

shows that the uncorrected figures of Lovelace, Fraser and Sease give results for the vapour pressure of the H_2SO_4 solutions which are in much better agreement with those of Grollmann and Fraser than the "corrected" figures, particularly over the lower concentration range, between 0.1 and 0.5 M, where the difference does not exceed 0.001 mm.

In view of these facts, the present authors suggest that the experimental data of Lovelace, Fraser and Sease for solutions of KCl should be regarded as the standard vapour pressure data throughout the whole concentration range.

Finally, in connection with the recently published work of Robinson on zinc and cadmium chlorides⁸ it is desired to place on record that one of the present authors (J. E. G.) has been engaged since early in 1938 in the measurement of the vapour pressure of solutions of both zinc and cadmium chlorides by the dew point method. The work on $CdCl_2$ is almost complete, and that on $ZnCl_2$ in an advanced stage of preparation.

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⁸ *These Trans.*, 1940, 36, 747, 1135.

IONIC DIAMAGNETIC SUSCEPTIBILITY AND DIAMAGNETIC CORRECTING CONSTANTS.

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The diamagnetic susceptibility of a polar salt may be considered as an additive function of the susceptibility of its ions, the ions being regarded as independent centres of diamagnetism, thus

$$\chi_M = \chi_{cation} + \chi_{anion}.$$

The contribution of the ions to the diamagnetism has been estimated by a variety of methods by different investigators from the experimentally determined molar susceptibilities of compounds. Starting from the alkali halides, the most strictly polar salts, tables of the diamagnetic

susceptibility of ions have been prepared. The literature shows a considerable divergence among the values proposed by different observers. Each investigator tends to employ his own standard set of values so that correlation of magnetochemical work is rendered difficult. It appears therefore that a comparative survey of the methods available is required, calculating the ionic diamagnetic susceptibilities from such trustworthy experimental data as is available. In this way an average set of ionic susceptibilities can be obtained.

There are two important reasons for establishing such a standard set of values. Firstly, to compare with the various theoretical values for the magnetic susceptibility of ions and secondly to obtain a set of ionic correcting constants for use in estimating the diamagnetic effect of such ions in work with paramagnetic molecules. For compounds of low paramagnetic susceptibility the diamagnetic correction is often of appreciable size so that as great a degree of accuracy as possible is desirable. A table of some of the ionic magnetic susceptibilities proposed by different authors is given in Bhatnagar's "Magnetism," page 142, and reference to this will show the considerable variation between the values. Although in a number of cases agreement is fair, in extreme cases (e.g., Cs^+) variations reach as much as ten units of molar susceptibility.* Stoner ("Magnetism and Matter," p. 272) has proposed a set of ionic correcting constants based on a method due to Brindley, and employing experimental measurements due to Kido, but it seems more justifiable to attempt to obtain an average set of values using as wide a range of methods and experimental data as possible. It will be seen from what follows, that when allowance is made for possible sources of error in the methods, and values are re-calculated using improved experimental results, an extraordinarily good agreement is found for the ionic susceptibilities of the alkali metal and halide ions by the different methods. From these, values for the other ions can be deduced wherever reliable experimental data is available. In many cases, however, such values can only be given approximately until further measurements are available so that possible sources of error in the measurements of individual compounds may be eliminated. Having obtained the ionic values a comparison can be made with the various theoretical ionic susceptibilities. Further, it is possible to make a comparison between the ionic susceptibility values and those for the atom combined in homopolar compounds.

The earliest estimates of atomic susceptibilities were due to Pascal^{1†} and are based on his measurements of the susceptibility of halogenated carbon compounds. Such compounds all contain a homopolar bond between the atom in question and the nearest carbon atom so that this bond effect will be included in the estimated susceptibility, as has been pointed out by Stoner and others. Pascal's atomic susceptibility values are, thus, those of the atom in its homopolar compounds and not the value for the free ion. Pascal has shown that there is a definite constitutive bond effect in many organic compounds and Gray² and his

* Throughout the paper, magnetic mass susceptibilities are expressed in units of Gram-Ionic, or Molar, Diamagnetic susceptibility, i.e., $-\chi_M \times 10^6$.

¹ P. Pascal. A summary of references to Pascal's work is given in Stoner, "Magnetism and Matter," p. 496.

[†] A summary of these values will be found in the *International Critical Tables*, Vol. VI, p. 349.

² F. W. Gray and W. Cruickshank, *Trans. Far. Soc.*, 1491, 1935.

co-workers have supplied evidence that a single homopolar bond will have an appreciable depressing effect on the total molar susceptibility. Thus susceptibility values for halogen atoms derived from homopolar compounds will be lower than the corresponding ionic ones, while those for cations will in most cases be higher since they are derived from the halide value. Comparison of strictly ionic susceptibilities with Pascal's homopolar values gives the bond effect for each atom, i.e., the lowering of susceptibility of the ion on passing from the free ion to an atom held by a homopolar bond.

Ionic Susceptibilities for Halide and Alkali Metal Ions.

The first method employed here for calculating ionic susceptibilities does not appear to have been suggested previously. This is to estimate from Pascal's experimental susceptibilities of the halogen molecules a value for the ionic susceptibilities of the halide ions by making use of the ratio between theoretical and experimental susceptibilities. Slater's³ theoretical method for calculating magnetic susceptibilities is employed in preference to other theoretical methods, since, on the whole, for the medium range of atomic numbers it gives results in best agreement with experimental data. For the very light and very heavy ions there is considerable discrepancy between all the theoretical values and those found by experiment. Such discrepancy is, however, an absolute one and will not affect the ratio ion/atom.

By taking one half of the molecular susceptibility of the halogen molecules one obtains Pascal's homopolar atomic susceptibility of the

halogen atoms. This may be converted to a true ionic susceptibility by using the ratio $A/B = C/D$ where A = the theoretical atomic susceptibility corresponding to the above experimental value, and is obtained by taking one half of the theoretical magnetic susceptibility of the molecule. (Reference to "Magnetism and

TABLE I.

Halogen.	Theoretical Magnetic Mass Susceptibility.		Experimental Magnetic Mass Susceptibility.	
	Homopolar Atom. (A.)	Ion. (C.)	Homopolar Atom. (B.)	Ion. (D.)
Fluorine .	7.1	8.30	6.3	7.3(5)
Chlorine .	22.3	25.79	20.2	23.4
Bromine .	35.4	40.01	32.0	36.2
Iodine .	53.0	59.80	45.7	51.6

Matter" by Stoner, p. 467, will give details of the method for calculating a theoretical molecular susceptibility for the halogens); B = the experimental homopolar atomic susceptibility as above; C = the theoretical ionic susceptibility calculated by Slater's method; D = the required experimental ionic susceptibility. Table I shows in columns 2, 3 and 4 the values of A , B and C for the halogen atoms while column 5 gives the resulting value for D . This method is not applicable to the alkali metal ions.

Methods 2, 3 and 4.—Three methods due to Weiss⁴ are available for estimating ionic susceptibilities. The first of these corrects Pascal's atomic values for the homopolar bond effect by adding or subtracting a constant factor ± 3.0 units of molar susceptibility. In addition, from the evidence of refractivity data and its correlation with magnetic susceptibility data, he corrects for the deforming effect of adjacent ions in the compound. These values of Weiss are employed as they stand in

³ J. C. Slater, *Physic. Rev.*, 1930, 57.

⁴ P. Weiss, *J. Physique*, 1930, 1, 185.

the present paper, although it should be pointed out that the value of the bond effect for all ions is by no means constant. As will appear later, this effect increases with increasing atomic number of the ion. The values for the ionic susceptibilities of halide and alkali ions by this method are shown in Table II, column 2.

Accurate measurements of the diamagnetic susceptibilities of certain of the alkali halides have been made by Hocart⁵ and from these Weiss deduced ionic values for the halide and alkali metal ions concerned. Having shown that the hydrogen ion has an effective paramagnetism in solution of 1.2 units of molar susceptibility, he deduced a value for the ionic susceptibility of the chloride ion as a starting point, other values then following from this, with allowance as in the previous method for the deforming effect of adjacencies. These values are shown in column 3 of Table II.

Yet another method due to Weiss³ makes use of Reicheneder's⁶ measurements of the magnetic susceptibilities of the halogen acids from which the correction for the effective paramagnetism of the hydrogen ion gives the ionic susceptibilities of the halide ions. Experimental values for these acids have more recently been obtained by both Kido^{7a} and Farquharson⁸ and taking a mean of the values due to all three authors gives a slightly different figure for the ionic susceptibilities than that of Weiss. Table III gives the relevant data, the ionic susceptibilities for the halide ions being shown in the last column. The method is, of course, inapplicable to the alkali metals

TABLE II

Ion.	Gram-Ionic Susceptibilities.			
	Weiss-Pascal.	Weiss-Hocart.	Brindley-Hoare.	Kido.
Fluoride .	—	—	9.4	12.2
Chloride .	23.1	23.1	24.2	22.1
Bromide .	34.7	33.9	34.5	34.7
Iodide .	49.8	49.5	50.6	53.2
Lithium .	—	—	0.7	—
Sodium .	7.6	8.2	6.1	7.6
Potassium .	16.0	16.5	14.7	13.6
Rubidium .	24.3	—	22.0	27.2
Caesium .	41.0	—	35.1	41.0

TABLE III

Ion.	Molar Susceptibility Halogen Acid.				Gram-Ionic Susceptibility.
	Reicheneder.	Kido.	Farquharson.	Mean Value.	
Chloride . .	21.9	21.9	23.0	22.3	23.5
Bromide . .	32.5	34.6	31.4	32.8	34.0
Iodide . .	50.2	(53.5) *	49.3	49.9	51.1

* Neglected as too high.

Methods 5 and 6.—A fifth and sixth method of estimating ionic susceptibilities are both due to Brindley, the latter in collaboration with Hoare. In the first of these methods Brindley⁹ improves on a method suggested by Joos and used by Ikenmeyer. The contribution to the

⁵ R. Hocart, *C. Rend.*, 1929, 1151.

⁶ K. Reicheneder, *Ann. Physik*, 1929, 58.

⁷ (a) K. Kido, *Sci. Rep. Tohoku Univ.*, 1932, 149; (b) *ibid.*, 1932, 288; (c) *ibid.*, 1932, 869.

⁸ J. Farquharson, *Phil. Mag.*, 1931, 283.

⁹ G. W. Brindley, *ibid.*, 786.

total susceptibility of anion and cation in ions of the inert gas configuration, *i.e.* NaF, KCl, RbBr and CsI, are considered by Joos to be inversely as the square of the nuclear charge. Brindley showed that a more accurate estimate is given by using the ratio $1/(Z-s)^2 : 1/(Z'-s')^2$, where Z and Z' are the respective nuclear charges and s and s' are the screening constants given by Slater's method for determining atomic susceptibilities. The appropriate values of Z , s and Z' , s' are employed for each electron shell, and using Slater's effective quantum numbers for the respective shells, Brindley estimated the proportion of the experimental susceptibility due to each ion from the expression:—

$$\chi_{\text{cation}} = \frac{\Sigma \bar{r}^2_{\text{cation}}}{(\Sigma \bar{r}^2_{\text{cation}} + \Sigma \bar{r}^2_{\text{anion}})}, \text{ where } \Sigma \bar{r}^2 = \frac{(n')^2(n' + \frac{1}{2})(n' + 1)}{(Z - s)^2}.$$

$\Sigma \bar{r}^2$ represents the electron density distribution summed for each electron shell, and n' = the effective quantum number of the shell. Values for the ionic susceptibility of the alkali and halide ions as well as others of inert gas configuration are obtained in this way. In the present paper Ikenmeyer's values have not been included, as they are not accurate enough for the present purpose. Experimental measurements of the molar susceptibility of the alkali halides of required configuration have up to date been made by Hocart,⁶ Kido,^{7a} Gray and Farquharson^{10a} Gray and Dakers^{10b} and by Brindley and Hoare.¹¹ Comparison of these values showed that those of Hocart and of Brindley and Hoare were in best agreement and these have been used in the present paper as more reliable than some of the others. The final ionic values given in columns 6 and 7 of Table IV thus vary slightly from those obtained by Brindley in his original paper on this method and also from those calculated by Stoner¹² from Kido's^{7a} experimental values. Further evidence for considering Hocart's and Brindley and Hoare's values as more reliable than those of other workers is considered later on in this paper. The values of $\Sigma \bar{r}^2$ required for this calculation are shown in columns 2 and 3 of Table IV, while the experimental halide values are shown in columns

TABLE IV

Inert Gas Configuration.	$\Sigma \bar{r}^2$.		Experimental Molar Susceptibilities.		Gram-Ionic Susceptibilities.	
	Cation.	Anion.	Hocart.	Brindley.	Cation.	Anion.
NaF	5.28	10.27	—	15.9	5.4	10.5
KCl	—	—	39.1	38.8	15.0	23.9
RbBr	32.03	49.73	—	56.4	22.2	34.3
CsI	50.09	74.19	—	85.7	34.6	51.1

4 and 5. The actual experimental figure for caesium iodide has had 3.1 units of susceptibility added to correct from 8-co-ordination to 6.

Subsequently to Brindley's first paper, Brindley and Hoare¹¹ proposed a slightly different set of standard ionic values based on careful experimental measurements of the susceptibilities of the crystalline salts of the alkali halides. Ionic values were deduced from these by assuming that in the case of the lightest ion of the series, lithium, the experimental susceptibility might be taken as the same as the theoretical, calculated

¹⁰ (a) Gray and Farquharson, *Phil. Mag.*, 1930, 191; (b) Gray and Dakers, *ibid.*, 1931, 81.

¹¹ Brindley and Hoare, *Proc. Roy. Soc.*, 1935, 325.

¹² Stoner, "Magnetism and Matter," p. 271.

by Slater's method. Since the theoretical value for this ion is small ($\chi_M = -0.72 \times 10^{-6}$) any small divergence between theoretical and experimental values will not appreciably influence the values for other ions derived from this starting point. This extensive investigation showed that slightly different ionic values for any one ion were obtained for crystalline salts of different co-ordination number, increasing co-ordination causing a slight fall in diamagnetism due to deformation of the outer electron orbits. Thus, in the case of caesium iodide the increase from the normal 6-co-ordination of the other alkali halides to 8-co-ordination was shown by Brindley and Hoare to be accompanied by a fall in susceptibility of 3.1 units on the total molar susceptibility. The ionic correcting constants obtained by Brindley and Hoare for salts of 6-co-ordination have been employed throughout this present paper as they are in closest agreement with ionic values obtained by the other methods. This method is open to the objection that the choice of lithium as standard is not an ideal one since for the very light ions it has been shown that the theoretical susceptibilities are considerably too low. It is not until the ions of atomic numbers of the order ten to eighteen are reached that the theoretical and experimental susceptibilities approach each other (see Fig. 5). Thus the use of the lithium ion as standard will make the susceptibilities of negative ions derived from it slightly too high but the error is not large since the susceptibility of the lithium ion is itself so small. Table II, column 4 shows the relevant figures for ionic susceptibilities obtained by this method.

Method 7.—Kido⁷ has more recently suggested another approach to the problem. From a large number of measurements of the molar susceptibilities of polar salts he has plotted curves in which salts in the same group of the periodic table with a common anion are compared. When the molar susceptibility is plotted against the number of electrons in the cation for series with the same anion Kido finds that a series of straight lines result. In this way the alkali halides give a set of parallel straight lines. By extrapolation to the value effective atomic number 0, he deduces a value for the anion assuming that the susceptibility of the hydrogen ion can be taken as zero, *i.e.*, the extrapolated value is that

corresponding to the acid H^+A^- and taking H^+ as zero gives the anion value required. This method is open to two sources of error, for as Weiss has shown, the effective paramagnetism of the hydrogen ion should be allowed for in estimating ionic susceptibilities and, even more important, it can be shown that the smoothing out of the susceptibility values to a straight line is not justified. Not only are the experimental susceptibilities not a linear function of the number of electrons in the cation or anion, but the theoretical susceptibilities themselves show a definite divergence from a linear form. This point is discussed more fully later. The magnitude of the error introduced in this way is for most ions not large, so that Kido's values are included in calculating the present average values. Column 5 of Table II shows Kido's values.

Summary of Results by foregoing Methods.

Comparison of the ionic values in the last columns of Tables I, III and IV with those in Table II shows that for the chloride, bromide and iodide ions these methods give a remarkably good agreement so that a satisfactory mean can be calculated for these three ions. Kido's value for the iodide ion has been omitted from the values used as being obviously too high. Thus an average for these ions results as follows:—

Ionic susceptibility	$\text{Cl}^- = 23.4 \pm 1.3$ (mean of 7 values).
„ „	$\text{Br}^- = 34.6 \pm 1.6$ (mean of 7 values).
„ „	$\text{I}^- = 50.6 \pm 1.6$ (mean of 6 values).

For the fluoride ion, data is more limited and agreement not so good and it again appears likely that Kido's value of 12.2 is too high. A mean of the remaining values gives :—

Ionic susceptibility $F^- = 9.1 \pm 1.8$ (mean of 3 values).

The data for the alkali ions is also rather restricted and agreement is not as close as for the first three halide ions, but the following mean values result :—

Ionic susceptibility $Na^+ = 7.0 \pm 1.7$ (mean of 5 values).

“ “ $K^+ = 15.1 \pm 1.4$ (mean of 5 values).

“ “ $Rb^+ = 22.8 \pm 1.5$ (mean of 3 values).

“ “ $Cs^+ = 37.9 \pm 3.3$ (mean of 4 values).

Kido's values have again been neglected in calculating the susceptibilities of the rubidium and caesium ions as being much higher than the other values.

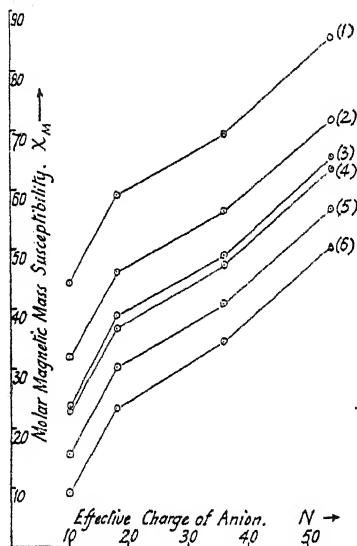


FIG. 1.—Experimental susceptibilities of alkali halides and the halide ions plotted against effective charge of anion.

- (1) Caesium salts (Brindley and Hoare).
- (2) Rubidium salts (Brindley and Hoare).
- (3) Potassium salts (Brindley and Hoare).
- (4) Ammonium salts. (This Laboratory.)
- (5) Sodium salts (Brindley and Hoare).
- (6) Mean experimental susceptibilities for halide ions (present paper).

Since the alkali values are only given by some of the methods and the agreement is not as close as is desirable it was considered advisable to use the summarised halide values to obtain a more accurate set of values for the alkali ions. This was done by means of a graphical method introduced to eliminate individual experimental errors in the susceptibility measurements used. If the experimental susceptibilities for the alkali halides obtained by the various authors mentioned previously are plotted against the effective atomic number of the anion it at once becomes apparent that the values of Brindley and Hoare and of Hocart are for the most part the most satisfactory. For the halide series of the alkali metals these authors' results give graphs which, although not linear throughout, are parallel over the corresponding section on passing from one halide value to the next (see Fig. 1). Values of other observers in many cases showed deviations from this parallel relationship. This graphical representation thus serves as an excellent check on the accuracy of the experimental figures as well as a means of smoothing out any individual deviations for a given compound. Plotting below the halide salt values the above mean values for the halide ion gives the susceptibilities for the

various alkali ions from the average distance between the graphs for the corresponding parallel sections. The values obtained in this way are likely to possess considerably greater accuracy than those based on individual measurements. The graphical values result as follows:—

$$\text{Na}^+ = 6.6, \quad \text{K}^+ = 14.7, \quad \text{Rb}^+ = 22.2, \quad \text{Cs}^+ = 35.0.$$

A mean of these graphically obtained values and the original set gives a final set of alkali ionic values proposed as the most accurate that can at present be obtained:—

Ionic susceptibility	$\text{Na}^+ = 6.8.$
„	„ $\text{K}^+ = 14.9.$
„	„ $\text{Rb}^+ = 22.5.$
„	„ $\text{Cs}^+ = 35.0.*$

The ionic susceptibility of the lithium ion, being small, is difficult to estimate since the possible deforming factors in the crystalline salts will have their maximum effect. Brindley and Hoare, recognising this deformation in the experimental values, employed the value $\text{Li}^+ = 0.7$, assuming agreement between theoretical and experimental susceptibilities. Since, however, the theoretical susceptibility becomes increasingly lower than the experimental for the lighter ions it is likely that this is too low a value. Brindley's inert gas configuration method of finding ionic susceptibilities although not directly applicable can be modified for this case. By calculating an ionic value for the lithium ion from the salts LiF , LiCl , LiBr , where the ions are of unequal configuration, and extrapolating back to the symmetrical structure (*i.e.* the hypothetical LiX , where X would have a structure similar to the H^- ion and thus LiX would correspond to twice the helium configuration), it is possible to obtain a value for the lithium ion. This method gives an ionic susceptibility for Li^+ from lithium bromide = 0.565, from the chloride = 0.598, from the fluoride = 0.766, whence, plotting these figures against the atomic number of the inert gas configuration attained in each compound and extrapolating back, a value for the lithium ion of ionic susceptibility $\text{Li}^+ = 1.2$, with an uncertainty of some 0.2 units, is obtained.

This value is confirmed by using the new fluoride ion value and Brindley and Hoare's lithium fluoride experimental value, which is the least likely to suffer from deforming effects owing to the more nearly equal size of the two ions than in other compounds. Since the experimental susceptibility of lithium fluoride is 9.1 a value for $\text{Li}^+ = 1.0$ results from this method. The values of the other lithium halides cannot be similarly used, for the distortion produced by the unequal size of anion and cation makes it impossible to obtain a value. It is proposed provisionally to take 1.0 as the most likely value for the ionic susceptibility of the lithium ion.

Ionic Susceptibilities of Other Ions.

These new ionic values can be employed to obtain ionic susceptibility values for other ions provided that polar salts are used and the susceptibility is assumed additive. Stoner in "Magnetism and Matter," page 272, has given a set calculated by him from Kido's measurements of salts, using the halide and alkali metal ionic values obtained by Brindley's first method. Kido⁷ has also suggested a number of values from his own measurements but for the reasons already given it is proposed to attempt to obtain values of greater accuracy. In the various cases now considered for which ionic values are suggested an average of the best experimental values has been taken to avoid errors of individual experimentors and

* The two high values of 41.0 have been omitted in calculating this mean, since the graph supports the lower values.

wherever possible the graphical means of smoothing out individual discrepancies, due to the deforming factors already referred to, have been used. In this way values for the ionic susceptibilities of the univalent nitrate, oxyhalogen and cyanide series of negative ions have been calculated and for the positive ammonium and thallium ions. The data used is that due to Kido, to the present author and some unpublished work being completed in these laboratories by Miss M. E. Bedwell. Since correcting constants are frequently needed for the commoner polyvalent anions the values for some of these are included in the present paper. It should be noted, however, that such values are only strictly applicable for these ions in combination with univalent cations. Brindley has pointed out that on passing from univalent to divalent cations the susceptibility of the anion does, in the case of some salts, become modified, *e.g.*, the effective susceptibility of the halide ions in the alkaline earth halides is less than in the alkali series. It is proposed to consider the necessary modifications to be introduced in the present values when combined with polyvalent cations in a subsequent paper.

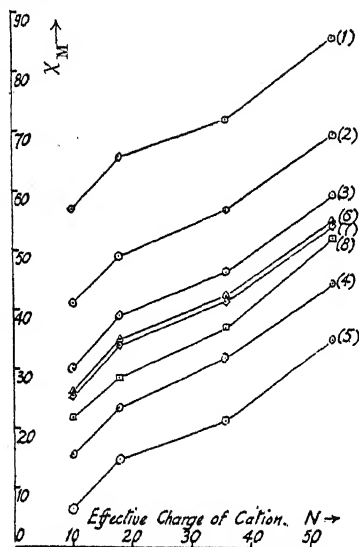


FIG. 2.—Experimental susceptibilities of alkali salts and the alkali ions plotted against effective charge of cation.

- (1) Alkali iodides (Brindley and Hoare).
- (2) Alkali bromides (Brindley and Hoare).
- (3) Alkali chlorides (Brindley and Hoare).
- (4) Alkali fluorides (Brindley and Hoare).
- (5) Alkali ions—Mean experimental susceptibilities (present paper).
- (6) Alkali sulphates (various authors).
- (7) Alkali nitrates (various authors).
- (8) Alkali carbonates (various authors).

The method of calculating the ionic susceptibilities in this section is as follows:—

Nitrate Ion.—The available experimental values for nitrates are those due to Kido ^{7a} who has measured the susceptibilities of the nitrates of the alkali metals and nitric acid. On plotting these values against the number of electrons in the anion they do not fall on the simple straight line which Kido suggested, but if similarly plotted between Brindley and Hoare's ¹¹ corresponding values for the alkali fluorides and chlorides (see Fig. 2, curve 7) do, over the range sodium to rubidium, run parallel with the halide graphs. This gives evidence for the reliability of these values for determining the susceptibility of the nitrate ion. Kido's experimental value of 22.7 for lithium nitrate is not included since the value it gave for the nitrate ion was considerably higher than the mean obtained from the graphical method. From the graph the mean susceptibility of the nitrate ion is:—

$$\text{Ionic susceptibility } \text{NO}_3^- = 18.9.$$

Kido's own value of 20.1 is probably too high, due to including the lithium value and to considering the graph as a straight line. It may be noted

in passing that this graph may be used to give an estimate of the susceptibility of caesium nitrate, a salt whose susceptibility has not up to the present been measured. The probable value for the susceptibility of this salt, corrected to 6-co-ordination, is 54.2 units of susceptibility.

Ammonium Ion.—A mean value for the susceptibility of this ion from Kido's experimental susceptibilities of the ammonium halides is far from satisfactory. A far better mean is given by the revised values obtained in this laboratory by Miss M. E. Bedwell. These not only give a closer agreement to the mean but on plotting between the values for the sodium and potassium ions (in Fig. 1, curve 4) show a similar parallel relationship which is by no means obtained with Kido's figures. Table V summarises the data employed, including the value for ammonium nitrate. The figures give a mean of 13.4 while the graph, without the nitrate value, gives 13.2, so that the mean value for the ionic susceptibility of the ammonium ion can be taken as 13.3 units.

TABLE V.

The Oxyhalo-

gen Ions.—Kido¹² and the present author¹³ have obtained values for the molar susceptibilities for several of the alkali salts of the chlorate, bromate, iodate, perchlorate and periodate ions which, except for the perchlorate ion, are in agreement. Here Kido's value is rather lower (see Table V). In all

Salt.	Molar Susceptibility.		Gram-Ionic Susceptibility.	
	Kido.	Bedwell.	Kido.	Bedwell.
NH ₄ F .	24.5	23.0	15.4	13.9
NH ₄ Cl .	34.2	36.7	10.8	13.3
NH ₄ Br .	47.4	47.0	12.8	12.4
NH ₄ I .	66.0	64.0	15.4	13.4
NH ₄ NO ₃ .	33.6	32.6	14.7	13.7
	Kido.	Trew.	Kido.	Trew.
NaClO ₃ .	37.8	—	31.0	—
KClO ₃ .	—	44.3	—	29.4
KBrO ₃ .	53.2	54.1	38.3	39.2
KIO ₃ .	65.8	65.9	50.9	51.0
KClO ₄ .	45.1	48.1	30.2	33.2
KIO ₄ .	67.0	—	52.1	—

cases, except this latter, a mean of the values is taken, giving the following ionic susceptibility values: ClO₃⁻ = 30.2, BrO₃⁻ = 38.8, IO₃⁻ = 51.0, ClO₄⁻ = 33.2 and IO₄⁻ = 52.1. Further confirmation of these values was obtained by plotting the susceptibility of the potassium and thallium chlorates, bromates and iodates against the number of electrons in the anion as in Fig. 3 when two parallel curves result, which are almost straight lines. From these the average difference IO₃⁻ - BrO₃⁻ = 11.3 and BrO₃⁻ - ClO₃⁻ = 10.1, whence, if the value for the chlorate ion is taken as 30.2, that for the bromate becomes 40.4 and for the iodate 51.7. While the iodate ion value is thus in fair agreement that for the bromate ion suggests that Kido's value for sodium bromate may be somewhat too low. A final mean for these three ions of ClO₃⁻ = 30.2, BrO₃⁻ = 39.8 and IO₃⁻ = 51.4 is suggested as being the most satisfactory.

An interesting point may be noted in this graph in that the usual points of inflection in the halide-effective atomic number graphs are so smoothed out by the addition of three oxygen atoms in the negative ion as to be almost missing, *i.e.* the three oxyhalides lie almost on a straight line, although the slight depression at the bromate ion is still noticeable.

¹³ Trew, *Trans. Faraday Soc.*, 1936, 1658.

Thus the anion behaves as a large compound ion in this series of compounds. This effect may be expressed as a bond depression due to a reduction of the spread of the electron density by the halogen oxygen bond. An estimate of the magnitude of this can be made from Pascal's atomic susceptibility value for the oxygen atom in combination, and this depression may be used to check the suggested susceptibility values for the perchlorate and periodate ions for which only limited data are available. It is reasonable to suppose that all four halide-oxygen bonds will have the same effect in depressing the susceptibility. Thus we have :—

$$\text{Ionic susceptibility } \text{Cl}^- = 23.4, \text{ClO}_3^- = 30.2.$$

Therefore the value for 3O-atoms = 6.8. But Pascal gives for the O-atom 4.6, whence the value for 3O = 13.8.

Hence the bond depression per Cl—O bond = $(13.8 - 6.8) = 2.3$. An exactly similar reasoning gives the depression for the Br—O bond = 2.9, and the I—O bond = 4.3. Values for the susceptibility of the

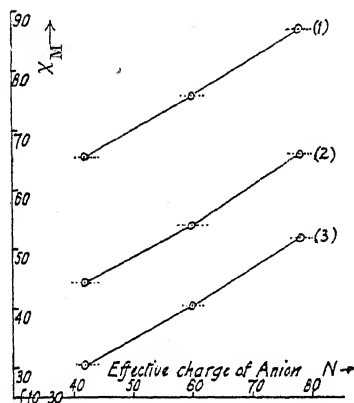


FIG. 3.—Oxyhalide salts of potassium and thallium plotted against effective charge of anion.

- (1) Thallium salts (present author).
- (2) Potassium salts (Kido and present author).
- (3) Mean experimental susceptibilities of oxyhalide ions.

perchlorate and periodate ions can then be estimated from these bond depressions as follows :—

$$\begin{aligned} \text{Ionic susceptibility}_{\text{ClO}_4^-} &= (\text{Ionic susceptibility}_{\text{ClO}_3^-} + \text{susceptibility O}^-) - \text{Depression Cl—O} \\ &= (30.2 + 4.6) - 2.3 \\ \therefore \text{ClO}_4^- &= 32.5. \end{aligned}$$

Similarly the value for $\text{IO}_4^- = 51.7$. The agreement with the values obtained previously is thus remarkably good and the ionic susceptibilities $\text{ClO}_4^- = 32.0$ and $\text{BrO}_4^- = 51.9$ are therefore proposed for these ions.

Thallium Ion.—With these values available it is possible to revise that for the thallium ion published in a previous paper.¹³ From the mean of the values for the fluoride, chloride, iodide (the latter corrected by adding on 3.1 to change from eight to six co-ordination), nitrate, chlorate, bromate and iodate salts of thallium given there, a mean ionic susceptibility value for the thallium ion of $\text{TI}^+ = 35.6$ is now obtained on the basis of these revised correcting constants. A confirmation of this figure can be obtained from Fig. 3, since the TI^+ and K^+ graphs are separated by a distance of 21.0 units. Whence, from the value 14.9 for the potassium ion, that of 35.9 results for the thallium ion. A mean value of $\text{TI}^+ = 35.7$ may finally be taken.

Cyanide, Cyanate and Thiocyanate Ions.—Ionic susceptibilities for these three ions have been given by the present author in a previous paper¹³ but these will require modification to bring into line with the

new values. Taking the above mean for the thallium ion the previously published values for these salts of thallium gives $\text{CN}^- = 13.3$, $\text{CNO}^- = 19.8$ and $\text{CNS}^- = 31.0$. These may be compared with the corresponding homopolar values due to Pascal,¹ namely, $\text{CN}^- = 10.8$, $\text{CNO}^- = 16.2$ and $\text{CNS}^- = 26.6$. Kido^{7b,c} has published values for the three ions based on measurements of some of the alkali cyanides, cyanates and thiocyanates. These values ($\text{CN}^- = 16.6$, $\text{CNO}^- = 23.9$ and $\text{CNS}^- = 37.5$) are considerably higher than the present ones and rather higher than seems reasonable than those of Pascal. It was therefore felt desirable to remeasure the susceptibilities of the alkali salts of these ions and as a preliminary a value was obtained using recrystallised A.R. potassium cyanide, which was tested and found to have a negligibly small iron content. A molar susceptibility = 27.2 was found. Subtracting the ionic susceptibility, 14.9, of the cation gives $\text{CN}^- = 12.8$ in reasonably close agreement with the value 13.3 obtained from the thallium salt. It thus appears likely that Kido's figures are too high. This is further supported by the difference between the homopolar and heteropolar values for this series, *i.e.* for $\text{CN}^- = 2.0$, $\text{CNO}^- = 3.6$ and $\text{CNS}^- = 4.4$, which are of the same order as those for the halide ion series. The values $\text{CN}^- = 13.0$, $\text{CNO}^- = 19.8$ and $\text{CNS}^- = 31.0$ are provisionally suggested for these three ions.

Divalent Anions.

Passing to divalent anions, values are proposed for the sulphate and carbonate ions.

Sulphate Ion.—Here it was found necessary to remeasure the molar susceptibilities of sodium and ammonium sulphates since Kido's values for these salts appeared too low, and, in addition, the susceptibilities of rubidium and caesium sulphate were measured, no previous value being recorded for these salts. Values were obtained as follows:—

$(\text{NH}_4)_2\text{SO}_4 = 67.0$; Na_2SO_4 (calculated from the decahydrate) = 52.4;
 $\text{Rb}_2\text{SO}_4 = 84.8$; and $\text{Cs}_2\text{SO}_4 = 110.3$.

These values, together with Brindley and Hoare's value¹¹ for lithium sulphate, Kido's value for potassium sulphate and the present author's for thallium sulphate, are plotted in Fig. 2, taking one half the molar susceptibility since two alkali cations are involved. The graph, Fig. 2 (6), falls extraordinarily satisfactorily between that for the chloride and fluoride ions, following exactly the same parallel relationship as do the halide ones. From the graph a mean value $\text{SO}_4^{2-} = 40.1$ can be obtained. It is not possible to assign a satisfactory value to the univalent acid sulphate ion HSO_4^- since the susceptibility of the potassium salt only has been measured. From this salt, for which the molar susceptibility is 49.8, we get $\text{HSO}_4^- = 34.9$, considerably lower than for the divalent ion. Further investigation of the susceptibility of other bisulphates is needed here, since this drop in susceptibility of more than 5 units is out of proportion.

Carbonate Ion.—For this ion the available molecular susceptibilities do not give as good an agreement as for the sulphate ion. However, plotting the experimental values of the alkali carbonates due to Pascal and Kido and the thallium salt values of the present author give, as before, a graph appreciably parallel to that for the other anions, when one half of the molar susceptibility is used. (See Fig. 2 (8).) Pascal's value for caesium carbonate appears from the graph to be anomalous and remeasurement of the susceptibility of this compound appears indicated. From the graph a mean value for the susceptibility of the carbonate ion $\text{CO}_3^{2-} = 29.5$ results.

Attempts to obtain values for the susceptibility of other ions such as PO_4^{3-} , AsO_4^{3-} were not proceeded with as the available experimental data

did not give any consistent values and it is obvious that further experimental measurements on salts of these anions is required. The possible

modifying influence of water of crystallisation and covalency of the molecule may also have to be allowed for here, *i.e.* the additive law may no longer hold for these more complex salts.

It may be useful at this point to summarise the new ionic values proposed, together with the Pascal homopolar values which correspond (Table VI.).

TABLE VI.

	Heteropolar or Ionic Susceptibility.	Homopolar (Pascal's) Susceptibility.
F ⁻ . .	9.1	6.3
Cl ⁻ . .	23.4	20.1
Br ⁻ . .	34.6	30.6
I ⁻ . .	50.6	44.6
Li ⁺ . .	1.0	4.2
Na ⁺ . .	6.8	9.2
K ⁺ . .	14.9	18.5
Rb ⁺ . .	22.5	27.2
Cs ⁺ . .	35.0	41.0

Values derived from above—

NO ₃ ⁻ . .	18.9	14.2
ClO ₃ ⁻ . .	30.2	—
BrO ₃ ⁻ . .	39.8	—
IO ₃ ⁻ . .	51.4	—
ClO ₄ ⁻ . .	32.0	—
BrO ₄ ⁻ . .	51.9	—
CN ⁻ . .	13.0	10.8
CNO ⁻ . .	19.8	16.2
CNS ⁻ . .	31.0	26.6
SO ₄ ⁼ . .	40.1	33.6
CO ₃ ⁼ . .	29.5	22.2
NH ₄ ⁺ . .	13.3	—
Tl ⁺ . .	35.7	—

Discussion of Results.

(1) **Comparison with Theoretical Values.**—Since some authors have attempted to show that a linear relationship exists between experimental ionic susceptibilities of the same series when plotted against the effective atomic number of the ion, it is useful to plot these values for the halide and alkali ions. In Fig. 4 the ionic susceptibilities of halide and alkali ions just obtained have been plotted, together with Pascal's corresponding values for the homopolar atom. All four curves are of the same type but

show a marked deviation from linearity and any attempt at smoothing out to a straight line is unjustified.

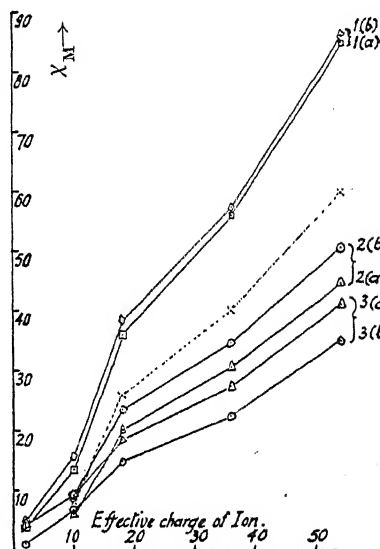
A further interesting comparison may be made with the inert gases. The sum of the anion and cation values for ions of the same inert gas configuration, or the sum of the corresponding alkali and halide atomic values of Pascal (given in the foregoing table) each gives the values for the electronic isomers corresponding to twice the inert gas structures. The mean values of the above molecular susceptibility are plotted in the uppermost curve (Fig. 4, curve 1(b)). It should be noted that the sum of the ionic values with that of the homopolar values is in extremely close agreement and shows the satisfactory nature of the present ionic values. Immediately below this curve are plotted (Fig. 4, curve 1(a)) the values for the experimental susceptibilities of the inert gases multiplied by two to bring to the same scale. (The values for the first three of these are due to Wills and Hector (Stoner, "Magnetism and Matter," p. 202) while the last two are as given in Klemm's "Magnetochemie," p. 145). It will be noted that the graph for the inert gas susceptibility follows the same general course as the previous ones but falls very slightly below that for the sum of the positive and negative atoms or ions, being almost exactly parallel with the latter as might be expected. The unequal nature of the charge in the isomer MX, *i.e.* (N - I) and (N + I) renders the total susceptibility slightly greater than where the two atomic centres are symmetrical. This is in agreement with

theory, since in the formula for the theoretical susceptibility a fall of one unit in N in the halide ion makes a relatively larger addition to $\Sigma\bar{r}^2$ than the lowering produced by the corresponding increase in N for the alkali ion.

To pass to a comparison of these experimental values with those obtained theoretically, Klemm in "Magnetochemie" gives graphs showing the course of the theoretical susceptibility-atomic number curve for alkali, halide and inert gas ions which show precisely similar deviations from linearity as the experimental curves. Klemm plots the theoretical values due to Angus¹⁴ which represent a slight modification of the Slater method. In Angus' method the s and p electrons for the same principal electron shell are considered separately in calculating the screening constants for the shell. The net result is to give rather lower theoretical susceptibility values which for the ions beyond potassium are in closer agreement with the experimental values. For

FIG. 4.—Experimental atomic and ionic susceptibilities of alkalis, halides and inert gases.

- (1a) Inert gas susceptibilities.
- (1b) Sum of halide and alkali susceptibilities both homopolar and heteropolar.
- (2a) Halide ion susceptibilities, homopolar (Pascal).
- (2b) Halide ion susceptibilities, heteropolar (present paper).
- (3a) Alkali ion susceptibilities, homopolar (Pascal).
- (3b) Alkali ion susceptibilities, heteropolar (present paper).
- Dotted curve. Theoretical values of Slater for comparison.



convenience of reference, the curve of the Slater theoretical values for the halide ions has been plotted on Fig. 4 (dotted curve). From this the similarity in shape between experimental and theoretical curves may be noted and in addition the fact that the theoretical curve rises more sharply than the experimental after atomic number 10. The theoretical curves for the alkali ions, the homopolar atoms and the inert gases show similar relationships to the corresponding experimental curves. The general form of these theoretical graphs is dependent on the Langevin equation for the diamagnetic susceptibility of a spherically symmetrical system, *i.e.* $\chi_A = -\frac{e^2 L}{6mc^2} \Sigma\bar{r}^2$, where $\Sigma\bar{r}^2$ is as defined under Brindley's

first method of calculating ionic susceptibilities. The change in the slope of the curve on passing from one ion to the next will be determined by the change in values of $\Sigma\bar{r}^2$ for all the shells. The net difference, in passing from one ion to the next in the series is thus made up of a positive and a negative increment, since the contributions of inner

¹⁴ Angus, *Proc. Roy. Soc.*, 1932, 569.

shells becomes progressively less as that of additional outer shells is added. Even where the number of added electrons is the same, *i.e.* in passing from Cl to Br and from Br to I, an analysis of the constituents of $\Sigma\bar{r}^2$ shows that these two factors are not the same. Thus an analysis of the constituents of $\Sigma\bar{r}^2$ brings out the real nature of the change in slope of the susceptibility-effective atomic number curve and shows that the non-linear nature of the curve is a theoretical necessity. The present survey bringing out similar effects in the experimental results

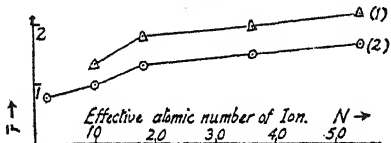


FIG. 4b.—Goldschmidt's ionic radii for alkali and halide ions plotted against effective charge of ion.

- (1) Halide ions.
(2) Alkali ions.

shows that in this respect experimental data supports the theory. Additional experimental evidence is supplied, if needed, by Fig. 4 (b), where Goldschmidt's¹⁵ ionic radii, derived from crystal structure data, for halide and alkali ions are plotted and show a similar type of deviation.

It is generally recognised that on the whole the theoretical susceptibilities are too high when compared with the experimental, the main deviations between experiment and theory occurring for the heavier ions where the theoretical values become progressively too high. (See

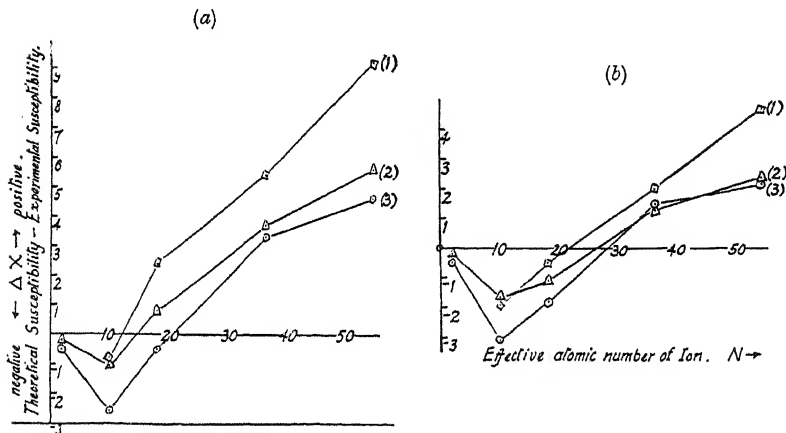


FIG. 5.—Deviations between theoretical and experimental susceptibilities.

- (a) Slater theoretical values { (1) Halide series.
(2) Inert gas series.
(b) Angus theoretical values { (3) Alkali series.

Stoner, "Magnetism and Matter," p. 272.) Klemm, however, suggests that any deviation between theory and experiment is not a systematic one but may be due to experimental error, especially since frequently there is a difference in the values obtained by different workers. In view of this opinion it was thought useful to plot the deviations between theoretical and experimental susceptibilities for the alkali, inert gas and halide ions, for both the Slater and Angus theoretical susceptibilities. Fig. 5 (a) and (b) shows these curves and indicates that the deviations are, contrary to Klemm's view, of a quite systematic nature. Thus,

¹⁵ Goldschmidt, *Trans. Faraday Soc.*, 1929, 253.

whichever theoretical susceptibilities are used, there is at first a fairly close agreement between theoretical and experimental values. The theoretical then falls below the experimental, reaching its minimum value at configuration $N = 10$, and then progressively rises with increasing values of N . The curves for the different ions are similar in type. The Slater values give best agreement for values of $N = 12-20$, while those of Angus are in better agreement for values of $N = 20-28$. On the whole, these curves support Stoner's opinion that Angus's separation of the "s" from the "p" electrons, in calculating the values, is not justified, since the Slater curves show the most systematic deviations. The deviations for heavier ions may be partly ascribed to the fact that experimental measurements never even approximate to the ideal condition of the free ion in empty space for which the theoretical calculations are made. Thus, as Brindley and others have pointed out, the limitation on the spread of the electron density for outer shells would lower the actually measured susceptibilities below the theoretical value. This effect is likely to become progressively larger, although not necessarily proportionately so as the volume of the ionic shell increases. That this is at least a partial explanation of the results is suggested by the gradual fall in susceptibility observed by Brindley and Hoare in compounds of increasing co-ordination number. It is further probable that for the elements of the alkali and halide groups agreement between theoretical and experimental susceptibilities would be reached could the experimental measurements be made for a single free ion in empty space, since Brindley and Hoare's results extrapolate back reasonably well to the Hartree theoretical value, as these authors have pointed out. This may not, however, be the case for all ions. The results obtained by the present author for the univalent thallous ion, where the experimental susceptibility is only a little more than half the theoretical value, suggests that in ions with the inert pair of electrons some other factor must be at work to produce the large discrepancy between experiment and theory.

(2) **Comparison of Heteropolar Values with Pascal's Homopolar Values.**—A useful comparison may be made for alkali and halide ions between Pascal's homopolar atomic susceptibility values and the present ionic values, thus giving a measure of the effect of converting a covalent to a polar bond. It will be noted from Table VI by subtracting corresponding values that the bond effect increases for the heavier ions. Plotting this bond increase or depression against N , the effective atomic number of the ion, shows in Fig. 6 the remarkably symmetrical nature of this effect, similar curves being obtained for halide and alkali ions over the corresponding sections. The general shape of these graphs and the gradual increase in bond effect on passing from lighter to heavier ion is in agreement with theory since the argument outlined before to explain the general form of the susceptibility-atomic number curve holds for these deviation curves. Furthermore, one electron makes a more marked contribution to the susceptibility in the higher shells, since the expression for Σf^2 contains several squared terms and thus the increasing bond effect is accounted for. The corresponding curve for the difference between theoretical homopolar and heteropolar values, derived by plotting the difference between the second and third columns of Table I (see Fig. 6 (1)) follows a similar course although some anomaly occurs at the fluoride ion. It may be remembered that only limited experimental data was

available for this ion and some correction in homopolar or heteropolar value may be needed. Fig. 6 further shows that Weiss's assumption that the Pascal atomic values can be corrected for the homopolar bond

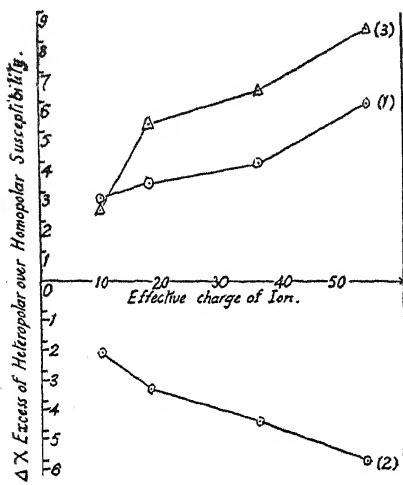


FIG. 6.—Excess of heteropolar over homopolar susceptibilities.

- (1) Halide ions.
- (2) Alkali ions.
- (3) Theoretical values halide ions.

effect by addition or subtraction of the factor ± 3.0 units of susceptibility is only approximately true for the lighter members of the series and a considerably greater correction is required for the heavier members. Fig. 6 summarises conveniently the extent of this bond effect for the univalent ions under consideration.

Summary.

1. Ionic diamagnetic susceptibility values for simple univalent ions of Periodic Table Groups I and VII, have been calculated. These may be used as correcting constants. These are mean values based on a survey of all the methods available, for calculating ionic susceptibility values, which have been critically discussed. A graphical method of checking experimental values, and deducing ionic correcting constants is introduced. Table VI gives the values proposed as the most satisfactory. Additional values for other univalent ions and some commoner divalent ions have been deduced from these, using a graphical means of smoothing out individual experimental errors.

2. The relationship between theoretical and experimental ionic susceptibilities for ions of related series has been considered graphically, showing that theoretical values follow substantially the same general form as experimental ones, but the relationship is not a linear one. The deviations between theoretical and experimental values have been discussed and it is shown graphically that, contrary to some opinions, such deviation is quite systematic.

3. The relationship between experimental values for the same atom in homopolar and heteropolar combination has been considered for the halide and alkali ions and it is shown that the bond effect due to the homopolar bond is, for the simple ions considered, not constant, but rises in a regular manner with increasing effective atomic number of the ion. The value for ions of the same effective atomic number is approximately of the same order of magnitude.

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BOND ENERGIES AND REPULSION ENERGIES IN PROTON-TRANSFER REACTIONS.

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In a reaction of the type $BC + A \rightarrow B + CA$ the necessary activation energy may be used either in stretching the bond BC, or in forcing the reactants BC and A closer together, thus facilitating the transfer of C. The actual course of the reaction will involve both these types of activation in such a proportion as to give the lowest possible activation energy. A number of writers have considered in particular cases the relative importance of bond energy (E_b) and interaction energy (E_i).¹

In the general case the most important contribution to E_i is from the interactions between A and C, and since these two atoms or groups approach to within a small distance of one another a large repulsion energy arises from the interpenetration of their electron shells. This interpenetration effect can only be treated very approximately, and the values calculated for the activation energy are rather sensitive to the exact assumptions made about the laws of repulsion.

In a proton transfer reaction, on the other hand, C represents a proton, which has no electron shell and thus exerts no repulsive forces of the type mentioned. If we write the reaction as $BH + A \rightarrow B + HA$ (where there is unit difference of charge between BH and B and between HA and A), then the only important contribution to E_i will be the interaction between A and B. In previous theoretical treatments of this type of reaction² it has been assumed that the energy of repulsion does not contribute to the activation energy, but that the centres A and B approach to a certain fixed distance during reaction without the expenditure of energy. It is the object of the present paper to replace this crude assumption by an approximate calculation of the part played by the interaction energy between A and B.

In reactions met with in practice the transfer of a proton takes place between two of the atoms C, N, and O. The bonds in $\geq CH$, $=NH$ and $-OH$ have very similar dissociation energies and Morse curves, and since the groups concerned all contain the same number of electrons the interaction forces should be similar in all cases. We have therefore considered for convenience the transfer of a proton between two identical centres, taken to be saturated carbon atoms.

¹ Eyring and Polanyi, *Z. physik. Chem., B*, 1931, 12, 279; Ogg and Polanyi, *Trans. Faraday Soc.*, 1935, 31, 604; Evans and Polanyi, *ibid.*, 1938, 34, 11; Hinshelwood, Laidler and Timm, *J. Chem. Soc.*, 1938, 848; Evans and Warhurst, *Trans. Faraday Soc.*, 1939, 35, 593.

² Horiuti and Polanyi, *Acta Phys. U.R.S.S.*, 1935, 2, 505; Bell, *Proc. Roy. Soc., A*, 1936, 154, 114; Bell and Lidwell, *ibid.*, 1940, 176, 114.

For the sake of symmetry we have also taken the case where one of them is negatively charged, *i.e.*, $\text{>CH} + \text{C}^- \rightarrow \text{>C} + \text{HC}^-$, since in this case the interaction between the carbons is the same in the initial and final states. This enables the problem to be treated by means of intersecting energy curves, while in the reaction between two uncharged molecules (giving rise to a positive and a negative ion) it would be necessary to use the more complex method of energy surfaces. All these restrictions could be removed at the expense of more laborious calculations, but the example chosen should be sufficient to indicate roughly the relative importance of bond energy and interaction energy.

The figure illustrates the energetics of the activation process. E_i represents the energy change involved in bringing the two carbon nuclei from an infinity to a distance r apart. The curve (a) represents the covalent binding of the link in >CH . When the reaction takes place the vibrational energy of this link is excited by an amount E_b , when

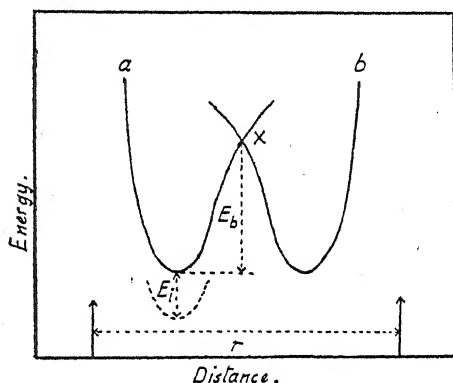


FIG. 1.

an adiabatic change takes place at the point X on to the similar curve (b). On account of the symmetry of the change this can take place without any alteration of energy or internuclear distance. The total activation energy E is then given by the sum $E_i + E_b$, and its value will depend on the distance r . For a particular separation r^* the calculated value of the activation energy will be a minimum, and this will correspond to the actual course of the reaction.

We have assumed that the energy is given by expressions having the following form

$$E = E_i + E_b \quad (1)$$

$$E_i = E_1 + E_2 = -\frac{\alpha e^2}{2r^4} + Pe^{-r/\rho} \quad (2)$$

$$E_b = D_0 \left\{ 1 - e^{-\alpha(1/r - 1/r_0)} \right\}^2 \quad (3)$$

The first term in equation (2) represents the polarisation induced by the charge on the ion, α being the polarisability of the uncharged group. We have taken the value for methane, $\alpha = 2.58 \times 10^{-24} \text{ cm}^3$, giving $E_1 = -2.94 \times 10^{-11}/r^4$, where (as in the other equations given) the energy is in ergs and the distance in Ångström units. The second term represents the repulsion energy between the electron shells. The exponential form used resembles the type of expression deduced theoretically, and for small interatomic distances it has been found to fit the results for the rare gases better than does an inverse power law.³ We

³ See Fowler and Guggenheim, *Statistical Thermodynamics*, p. 292, Cambridge, 1939.

have assumed that the values of P and ρ are the same as for uncharged molecules of similar electronic structure, *e.g.*, methane molecules. In this case the total interaction energy is given by

$$E_0 = -\frac{\mu}{r^6} + Pe^{-r/\rho} \quad (4)$$

The value of μ can be calculated theoretically for the rare gases, and Slater⁴ has given a semi-empirical expression in terms of the polarisability and the number of electrons in the outer shell which agrees well with the observed equation of state of many non-polar molecules, including methane.⁵ In our present units Slater's equation gives $\mu = 1.327 \times 10^{-10}$. There is no satisfactory basis for calculating P and ρ , but we can use experimental data on r_0 , the distance of closest approach of the two centres. Crystallographic data give 3.2–3.5 Å. as the distance of closest approach of two unlinked carbon atoms, while the van der Waals' treatment of the data for methane gas gives $r_0 = 3.56$ Å. from the equation of state and $r_0 = 3.24$ Å. from the critical constants. We have therefore used both $r_0 = 3.2$ Å. and $r_0 = 3.5$ Å. in making our calculations. Born and Mayer⁶ have found that the relation $r_0/\rho = 18$ applies well to a number of molecular lattices; on the other hand the crystal data for neon and argon give³ respectively $r_0/\rho = 13.0$ and $r_0/\rho = 13.8$.

We have taken the two values $r_0/\rho = 13.5$ and $r_0/\rho = 18$, and by combining these with the two values of r_0 and using the relation $(dE_0/dr)_{r=r_0} = 0$ we obtain four sets of values of P and ρ for use in calculating the interaction energies.

Equation (3) is the ordinary Morse equation for the link in >CH , and the appropriate constants can be obtained from spectrum data. We have taken $D_e = 7.19 \times 10^{-12}$ ergs, $\omega_e = 3160 \text{ cm.}^{-1}$, $r_e = 1.08$ Å, giving $a = 2.02 \text{ Å}^{-1}$; r^* , the separation corresponding to the minimum activation energy, is then calculated from equations (1)–(3) by the condition

$$(dE/dr)_{r=r^*} = 0,$$

and the contributions to the observed activation energy can be calculated from the same equations. The

CALCULATED ACTIVATION ENERGIES.

(Distances in Ångström units, energies in kcal/mole.)

	$r_0/\rho = 13.5$		$r_0/\rho = 18$	
r_0	3.5	3.2	3.5	3.2
r^*	2.59	2.57	2.85	2.74
E	18.8	14.6	23.4	22.2
E_b/E	0.68	0.82	0.88	0.84

adjoined table gives the calculated activation energies E , the separation r^* , and the fraction E_b/E which the bond energy contributes to the total activation energy. It will be seen that in each case the bond energy constitutes the major part of the activation energy. It is thus likely that previous treatments of proton transfer reactions, based purely on considerations of bond energies, are substantially correct, though the interaction energy

⁴ Slater and Kirkwood, *Physic. Rev.*, 1931, 37, 682.

⁵ Wohl, *Z. physik. Chem.*, 1931, *Bodenstein Festband*, 807.

⁶ Born and Mayer, *Z. Physik*, 1932, 75, 1.

would have to be taken into account in any accurate treatment of the problem. It is also of interest that the calculated activation energies all lie in the range 12-25 kcal./mole found experimentally for reactions catalysed by acids and bases, thus confirming the reasonableness of the model used.

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FOAM FORMATION AND FOAM STABILITY: THE EFFECT OF THE ADSORBED LAYER.

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It has long been realised that pure liquids never form a stable foam and that, of the factors necessary for stable foam formation, the presence of an adsorbed layer at the gas-liquid surface is of paramount importance.¹ Foulk² in his "balanced layer" theory seeks to explain the action of the adsorbed layer by attributing resistance to coalescence of adjacent bubbles in a foam to the molecular forces giving rise to adsorption; coalescence tending to produce a local equalisation of surface and bulk concentrations at the point of rupture of the separating lamellæ. It is, however, important that the film should possess what Gibbs has termed "elasticity,"³ to withstand mechanical shock. This has led to the suggestion^{1(a),4} that maximum foam occurs where surface tension is changing rapidly with concentration, the surface tension here being capable of speedy adjustment in response to small accidental changes in surface area. In this paper a variety of solutions including detergents, pure amphipathic substances and proteins, is investigated with a view to throwing fresh light on the nature and properties of the adsorbed layer and its relation to foam formation and foam stability.

Experimental.

Four main methods used by previous workers have been compared as follows:

a. Shaking Tube Method.

By this method a known volume of the liquid under test is shaken in a tube of standard size by some arbitrarily chosen means and the height and/or duration of the resulting foam measured.⁵ The main objection to this method is the difficulty of standardisation of technique. For convenience narrow tubes are usually used, and experiments on saponin

¹ Comprehensive summaries of the factors involved in foam formation and foam stability are to be found as follows: (a) Adam, 1938, *The Physics and Chemistry of Surfaces*, Oxford, 2nd edition, pp. 142 ff.; (b) Freundlich, 1922, *Colloid and Capillary Chemistry*, English translation, London, pp. 789 ff.; (c) Weiser, 1939, *Colloid Chemistry*, New York, pp. 313 ff.

² Foulk, *Ind. Eng. Chem.*, 1929, 21, 815.

³ Gibbs, *Collected Works*, 1928, 1, 300 ff. (cf. Adam, 1(a), 142).

⁴ Sasaki, *Bull. Chem. Soc. Jap.*, 1938, 13, 517.

⁵ (a) Trotman and Hackford, *J.S.C.I.*, 1906, 25, 104; (b) Watson, *ibid.*, 209; (c) Bartsch, *Kolloid-Beih.*, 1924, 20, 1; (d) Sasaki, *Bull. Chem. Soc. Jap.*, 1938, 13, 669.

solutions at 20° C., with tubes 25 cm. long and 17 mm. internal diameter, 10 c.c. of liquid and shaking for one minute by hand (*ca.* 150 shakes) gave results frequently reproducible to only 20 per cent. With solutions of poor foaming power experimental error was often as high as 100 per cent. Wall effects due to the small diameter of the tube were also pronounced with poor foaming solutions, and here bubbles were often of ill-defined shape making accurate measurements difficult or impossible.

b. Foam Number Method.

This is essentially a modification of the shaking tube method, but instead of measuring the height of foam, the volume of liquid not utilised in foam formation is measured, from which the percentage of the liquid in the foam (the "foam number")⁶ can be obtained. Saponin solutions gave results reproducible to *ca.* 15 per cent. by this method.

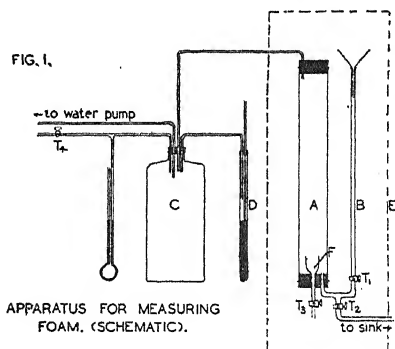
c. Observations on Single Bubbles.

The stability of single bubbles of standard size at the surface of the liquid under test has formed the basis of a method of studying foam.⁷ With saponin solutions reproducibility was poor (variations of 200 % and over were quite common) even when special precautions were taken to ensure cleaning the surface immediately prior to blowing the bubble, excluding draughts and as far as possible external vibrations, and preventing evaporation. With strongly foaming solutions the bubble life was excessively long. Another objection is that the results obtained are not necessarily indicative of the behaviour of a foam *in toto* as no account is taken of the stability of the lamellæ of liquid separating adjacent bubbles. Foulk and Miller⁸ used a modification of this method which approximates more nearly to the physical conditions of a foam, by measuring the stability of two juxtaposed bubbles blown from two opposed hollow hemispherical cups, and obtained results which were in good agreement with those obtained by the "porous septum" method (see (d) below).

d. Porous Septum Method.

Foulk and Miller⁸ measured the rate of formation of foam by a "dynamic foam meter" in which air was bubbled through a porous septum into a column of liquid contained in a *wide* tube.

The remaining experiments described in this paper were carried out by a modification of this method. A diagrammatic scheme of the apparatus is given in Fig. 1. The liquid under test is admitted to the large pyrex tube, A, 3 inches diameter and 3 feet length, through the side tube, B, care being taken to avoid excessive foam. The tap, T₁, is then closed, and the level of liquid in A adjusted to an arbitrarily chosen zero mark above the porous septum, F, by means of T₂. T₃ and T₄ are then closed, and the pressure inside A is reduced to 10 cm. of mercury below that of the atmosphere, by a water filter pump in series with a 10 litre bottle, C,



⁶ Preston and Richardson, *J. Physic. Chem.*, 1929, **33**, 1142.
⁷ (a) Hardy, *Proc. Roy. Soc., A*, 1912, **86**, 627; (b) Talmud and Suchowolskaja, *Z. physikal. Chem.*, 1931, **154**, 277.
⁸ Foulk and Miller, *Ind. Eng. Chem.*, 1931, **23**, 1283.

acting as stabiliser, and a constant pressure device, D. When a steady pressure difference is obtained air is admitted to the liquid in A through the porous septum, F, consisting of a sintered glass filter funnel 3.5 cm. diameter and pore diameter $15\text{--}40\mu$ (grade 3), by opening T_3 . In this way a column of foam is built up, the rate of intake of air being 1200 c.c. per minute (± 15 c.c.). The time required for the advancing foam front to rise 50 cm. is measured with a stop watch. This value, θ_{50} seconds, is an inverse measure of the foaming power of the liquid. When the column reaches the 50 cm. mark, T_3 is closed and any decay of foam is noted. T_4 is then opened and the pressure in A is immediately brought to that of the atmosphere, thus subjecting the foam to shock. Any decrease in foam level beyond 6.5 cm. (that allowed for by Boyle's law) is also noted. From these last two observations the stability of the foam can be assessed. A and B were enclosed in an air thermostat, E, and the temperature of the liquid inside was maintained with an accuracy of $\pm 1^\circ\text{C}$. Under these conditions values of θ_{50} were reproducible to 3.5 per cent.

A few results were obtained with a brass disc drilled with holes $1/64$ th inch diameter, in place of the sintered glass septum. This was particularly suitable with gelatin solutions.

The volume of liquid used for each experiment was one litre, and an attempt was made to use a smaller apparatus with 50 c.c. of liquid, using a tube 2 cm. diameter and a micro-sintered filter 9 mm. diameter. Reproducible results were not obtained owing to wall effects, and extreme sensitivity to small variations in pressure. Sasaki⁴ also carried out some early experiments with a small porous septum apparatus, but abandoned it later in favour of the shaking tube method.^{5(a)}

Measurements of surface tension (γ) were made by Adam's modification of the drop volume method.⁹ The age of surface during these measurements never exceeded one minute. *pH* determinations on gelatin solutions were made colorimetrically, and were frequently checked with the glass electrode. Viscosity measurements (η) on gelatin solutions were made with a calibrated bulb viscometer.

Purity of Materials.

The saponin was a standard batch of the triterpenoid glucoside type obtained from Messrs. C. W. Field, Ltd. The alkyl sodium sulphates were prepared from pure aliphatic alcohols of boiling range not greater than 2°C ., and with acetyl values mostly within 2 % (C_{14} compound—3 %) of the theoretical value. Sodium oleate was prepared from oleic acid from Messrs. British Drug Houses, Ltd., after conversion to the lead salt and redistillation of the acid, the acid value of the distillate being within 1 % of theory. Sodium ricinoleate and sulpho-ricinoleate were also obtained from B.D.H., and were similarly purified, except that the acids were not distilled. A variety of gelatins were obtained from Messrs. George Nelson, Dale and Co., Ltd., C. Simeon and Co., Ltd., and other well-known sources. De-ashing was carried out in one case by the method of Northrup and Kunitz.¹⁰

Results and Discussion.

Saponin.

Fig. 2 shows the effect of concentration of saponin on θ_{50} and γ at 20°C . At concentrations of 0.005 % and over it forms a stable foam which does not decay markedly even after 24 hours. Although it was possible to obtain a value for θ_{50} at 0.001 %, the foam consisted of large bubbles with extremely fragile walls which broke within 10 seconds of

⁹ Adam, see 1(a), pp. 376-382.

¹⁰ Northrup and Kunitz, *J. Gen. Physiol.*, 1928, 11, 477.

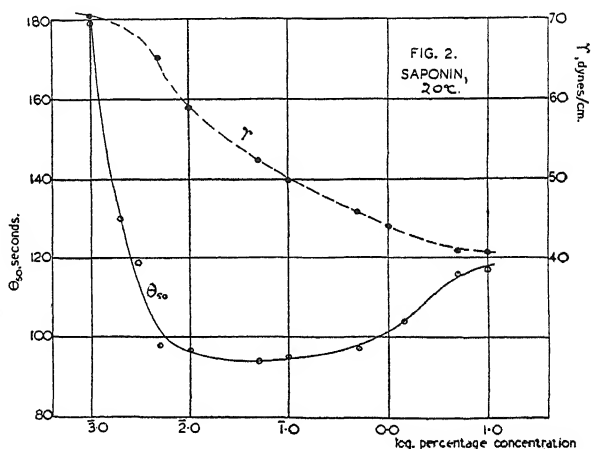
cutting off the air supply. Using an Adam-Langmuir trough, it was seen that between 0.005 and 0.001 % the characteristic elastic solid film of saponin loses much of its cohesion. Slight deterioration of foaming properties occurs above 0.1 %, probably due to surface crowding and crumpling of the film. For saponin solutions maximum foam is obtained where γ is varying appreciably with concentration.

The effect of temperature on the foaming of 0.01 per cent. solutions shows a marked deterioration between 30 and 35° C., it being impossible to obtain a column of foam higher than 35 cm. at the higher temperature. The foam so produced was extremely unstable, and collapsed within a few seconds of cutting off the air supply. Trough experiments failed to reveal any loss of cohesion. With 0.03 % solutions foaming deteriorated between 55 and 65° C., whereas with 0.07 % no variation of θ_{50} was observed up to at least 70° C.

Comparison between the standard saponin in 0.01 per cent. solution and seven other samples obtained from various sources gave values of θ_{50} and γ which

varied between 99 and 232 seconds and 58.9 and 66.0 dynes per cm. respectively. There was no simple correlation between these properties. The addition of various electrolytes (sodium, potassium, ammonium and calcium nitrates, sodium carbonate and borax) in 1.0 % solution

to 0.01 % of the standard saponin resulted in a slight increase in foaming power in each case, accompanied by a rise in γ of about four dynes per cm. The effect was small and indicates that the wide variations in θ_{50} and γ found with different samples are not likely to be due to electrolyte contamination.



Alkyl sodium sulphates.

Fig. 3 shows θ_{50} -concentration and γ -concentration relationships for four alkyl sodium sulphates with straight chains of 8, 10, 12 and 14 carbon atoms, at 38° C.

There are fairly well defined concentration ranges where foaming commences, *i.e.* C_{14} , 0.00025 N — 0.00065 N; C_{12} , 0.004 N — 0.01 N; C_{10} , 0.02 N — 0.04 N; C_8 , 0.03 N — 0.05 N. Between these concentrations γ is varying appreciably in every case. With the C_{14} and C_{12} compounds there are optimum concentrations where foaming is maximum, *ca.* 0.002 N and 0.02 N respectively. It will be seen that maximum foam occurs with the C_{14} salt at the critical micelle concentration, and therefore there is a simple correlation between θ_{50} and γ , as γ rises on either side of the critical concentration. With the C_{12} salt, however, maximum foam occurs at

about twice the critical micelle concentration, and here no such simple correlation is possible. No optima were observed with the C_{10} and C_8 compounds, probably because limited supplies of material made it impossible to investigate at concentrations much above $N/10$. It is concluded that, although at low concentrations where foaming commences, γ varies rapidly with concentration, at higher concentrations where foaming increases to a maximum the variation of γ with concentration may be slight.

The effect of sodium nitrate in 1 per cent. solution on θ_{50} and γ of dodecyl sodium sulphate is also shown in Fig. 3. The addition of this salt permits stable foam formation at about one-hundredth of the concentration at which the pure capillary active substance ceases to foam. This agrees with the findings of Adam and Shute¹¹ that the presence of ions common with the gegenions of paraffin-chain salts causes rapid

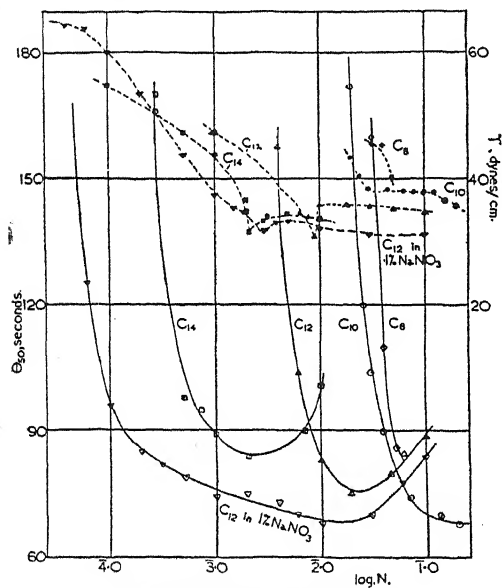


FIG. 3. n-ALKYL SODIUM SULPHATES, 38°C.
[θ_{50} full lines. γ broken lines.]

adsorption below the critical micelle concentration and emphasises the importance of the adsorbed layer in promoting foam formation. Table I shows similar results obtained with a commercial dodecyl sodium sulphate containing 60 per cent. $C_{12}H_{25}SO_4Na$, determined by titration against cetyl trimethylammonium bromide.¹²

As with the pure compound, the presence of a simple salt causes rapid adsorption of the paraffin-chain ions, giving rise to an increase in foaming power. The nature of the anion has little effect, but the kation is critical.¹³

Where adsorption is practically complete in the absence of added electrolyte, e.g. with 0.5 % commercial product, subsequent additions of sodium nitrate have little or no effect on θ_{50} or γ .

Commercial Wetting Agents.

Table II shows results obtained with a variety of commercial wetting agents and textile assistants in 0.01 and 0.1 % solutions. Determinations of the approximate percentage of active component of several of these were made by Adam and Hartley's method¹² where this was known to give a stoichiometric end-point. In some cases where this method was

¹¹ Adam and Shute, *Trans. Faraday Soc.*, 1938, 34, 758.

¹² Details of this method due to Adam and Hartley are to be found in Hartley and Runnicles, *Proc. Roy. Soc., A*, 1938, 168, 424.

¹³ Cf. Powney and Addison, *Trans. Faraday Soc.*, 1937, 33, 1258.

doubtful, and with the monosulphonated succinic esters which were known to be of fairly high purity, sodium estimations were made. In certain other cases details of purity were kindly supplied by the makers. These figures are also included in Table II, and with the values of θ_{50} and γ are of some use in assessing approximately the intrinsic effects of the various molecular structures in the formation and stability of foam.

The following broad conclusions may be drawn from Table II:

(1) The sulphated secondary alcohol, alkyl naphthalene sulphonates, sulphonated ether, oxycholesterol in sulphonated lorol, C-cetyl betaine and quaternary ammonium salts have similar foaming properties, although their capacities for lowering the surface tension of water vary within wide limits, e.g. 0.1 % alkyl naphthalene sulphonate, (D), and

TABLE I.—THE EFFECT OF ELECTROLYTES ON THE FOAMING PROPERTIES AND SURFACE TENSION OF COMMERCIAL DODECYL SODIUM SULPHATE, 38° C.

Electrolyte.	Concentration. %	θ_{50} .	Stability.*	γ .
0.025 % commercial product.				
—	—	195	Z	45.5
NaNO ₃	1.0	77	A	37.3
KNO ₃	1.0	160	B	40.5
„	1.88	150	A	39.3
NH ₄ NO ₃	1.0	82	A	38.3
Ca(NO ₃) ₂	1.0	134	Z	40.2
Na ₂ CO ₃	1.0	79	A	38.4
Na ₂ B ₄ O ₇	1.0	86	A	38.6
„	4.5	74	A	37.2
0.05 % commercial product.				
—	—	102	Z	37.9
NaNO ₃	1.0	73	A	34.1
0.5 % commercial product.				
—	—	75	A	31.6
NaNO ₃	1.0	75	A	30.1

* Stability of foam after cutting off air supply.

O = immediate collapse.

Z = collapse in two minutes.

B = very slight collapse.

A = no collapse in 15 minutes.

0.01 % oxycholesterol in sulphonated lorol, (H), have almost identical foaming properties yet H has a surface tension 13.5 dynes per cm. higher than D; similarly 0.01 % of the sulphated secondary alcohol, (C), has a similar foaming power to 0.1 % C-cetyl betaine, (M), yet there is a disparity in γ of 10.9 dynes per cm.

(2) The sulphated secondary alcohol of 12 carbon atoms promotes greater foam formation than the primary compound of 16 carbons. This is probably due to a marked tendency of the latter to hydrolyse, the solutions of which were turbid.

(3) The substitution of a hydroxymethylene group into the naphthalene nucleus, (F), in place of an alkyl (probably *iso*-propyl) group,

(D and E), greatly lowers the surface activity and does not promote foam formation.

(4) The sodium monosulphonates of succinic esters up to 16 total carbon atoms show little tendency to form a stable foam, even in solu-

TABLE II.—FOAMING PROPERTIES AND SURFACE TENSIONS OF SOME COMMERCIAL WETTING AGENTS. 38° C.

Sample.	Type.	Approx. Concentration of Active Component. (%)	Foaming Power (θ) and Surface Tension (γ).					
			0.01 %.			0.1 %.		
			θ .	γ .	Stability.	θ .	γ .	Stability.
A	Sulphated primary fatty alcohol (C ₁₈)	20	$\theta_4^* = 30$	57.5	O	$\theta_7^* = 60$	45.5	O
B	Ditto	40	$\theta_8 = 90$	54.8	Z	$\theta_{50} = 265$	36.0	B
C	Sulphated secondary fatty alcohol (C ₁₂)	60	$\theta_{50} = 80$	41.6	A	$\theta_{50} = 82$	28.4	A
D	Alkyl naphthalene sulphonate	20	$\theta_{27} = 88$	54.8	B	$\theta_{50} = 112$	32.3	A
E	Ditto	25	$\theta_{25} = 80$	65.9	B	$\theta_{50} = 85$	31.5	A
F	Hydroxymethylene naphthalene sulphonate	55	No foam	70.4	O	No foam	68.4	O
G	Sulphonated ether	—	$\theta_{50} = 95$	50.4	A	$\theta_{50} = 73$	27.4	A
H	Oxycholesterol in sulphonated lorol	—	$\theta_{50} = 110$	45.8	A	$\theta_{50} = 81$	27.9	A
I	Monosulphonated succinic ester (Na salt) $2 \times C_4$	91.5	No foam	63.7	O	$\theta_9 = 180$	46.9	A
J	Ditto	98.0	„	55.3	O	$\theta_{30} = 180$	36.8	A
K	Ditto	98.8	„	47.1	O	$\theta_6 = 15$	36.0	A
L	Ditto	86.7	$\theta_{50} = 233$	28.8	Z	$\theta_{50} = 72$	24.3	A
M	C-cetyl betaine	25	$\theta_{50} = 96$	52.2	A	$\theta_{50} = 80$	30.7	A
N	Quaternary ammonium salt	70	$\theta_{50} = 57$	39.2	A	$\theta_{50} = 60$	32.9	A
O	Ditto	90	$\theta_{50} = 88$	34.2	A	$\theta_{50} = 78$	32.4	A
P	Ditto	—	$\theta_{50} = 117$	55.1	A	$\theta_{50} = 70$	31.7	A

* θ_n , where n is less than 50, indicates that it was impossible to obtain a column of foam higher than n cm.

tions where γ is diminished by 30 dynes per cm. Only when a total of 20 carbons is present does foaming become appreciable, and then only in 0.1 % solution, the reduction in γ being over 45 dynes per cm. A

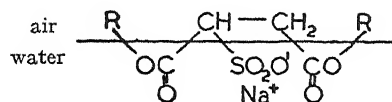


FIG. 4.—Orientation of a monosulphonated di-succinic ester at an air-water surface.

hydrocarbon chains of alkyl sodium sulphates, on the other hand, are capable of more orderly arrangement and, although not completely orientated into a condensed film, are likely to have greater cohesion than those of the dibasic ester molecules. It is probable that the reduction of cohesion impedes the formation of a stable foam.

Sodium Oleate and Related Compounds.

Additional evidence of the loss of foaming power incurred when molecules of the adsorbed layer are firmly anchored flat in the surface is shown by the effect of potassium permanganate on solutions of sodium oleate, and also of sodium ricinoleate and its sulphonated derivative (see Table III).

TABLE III

Solution.	0.001 M.			0.01 M.		
	θ_{50}	Stability.	γ	θ_{50}	Stability.	γ
Sodium oleate	108	A	24.6	78	A	23.5
Sodium oleate + equivalent KMnO ₄	183	B	43.9	120	A	25.1
Sodium ricinoleate	$\theta_6=25$	Z	44.5	130	B	32.3
Sodium sulpho-ricinoleate	$\theta_8=50$	O	42.6	$\theta_{40}=160$	Z	32.0

Sodium oleate alone produces a stable foam in 0.001 M and 0.01 M solutions, but the introduction of permanganate causes a marked deterioration of foam which is accompanied by a large rise in γ only with the weaker solution.

Adam and Jessop,¹⁴ have shown that the coherent monolayer of oleic acid on water was converted to the gaseous type by the introduction of permanganate into the substratum, the molecules of the monolayer becoming anchored to the surface by the double bond as well as the carboxyl. It therefore seems probable that the adsorbed oleate film, although not coherent, will become more perfectly gaseous by the formation of the dihydroxystearate and the subsequent loss of cohesion will diminish its foaming power. The results for sodium ricinoleate and sulpho-ricinoleate confirm this.

Gelatin.

Fig. 5 shows variations of θ_{50} , γ and η of three photographic gelatins with concentration at 38° C. The sintered glass septum was used for samples A and B, and the brass septum (see p. 497 above) for B and C. For A, B, and C there was an optimum foam concentration between 2 and 4 %. Below the optimum the curves rise steeply, and above it less steeply. There is no simple correlation between θ_{50} , γ , and η as these latter properties vary continuously between 0 and 10 %.

Comparison of some sixty commercial gelatins in 10 % solution gave values of θ_{50} ranging from 64 to 127 seconds, using the sintered glass septum, and here again there was no simple correlation with γ or η , although these varied between 43.5 and 53.3 dynes per cm. and 15 and 25 centipoises respectively.

Bogue,¹⁵ using the shaking tube method, found maximum foaming of 1 % gelatin to occur at the isoelectric point. With gelatins B and C maximum foam was observed slightly above the isoelectric point at pH 6, in 1, 3, 6 and 10 % solutions, also with gelatin A at 1 and 3 %. A

¹⁴ Adam and Jessop, *Proc. Roy. Soc., A*, 1926, 112, 367, 371.

¹⁵ Bogue, *J. Amer. Chem. Soc.*, 1922, 44, 1343.

was, however, anomalous in 10 % solution in that it showed *minimum* foam at pH 6, and in 6 % solution showed practically no variation between

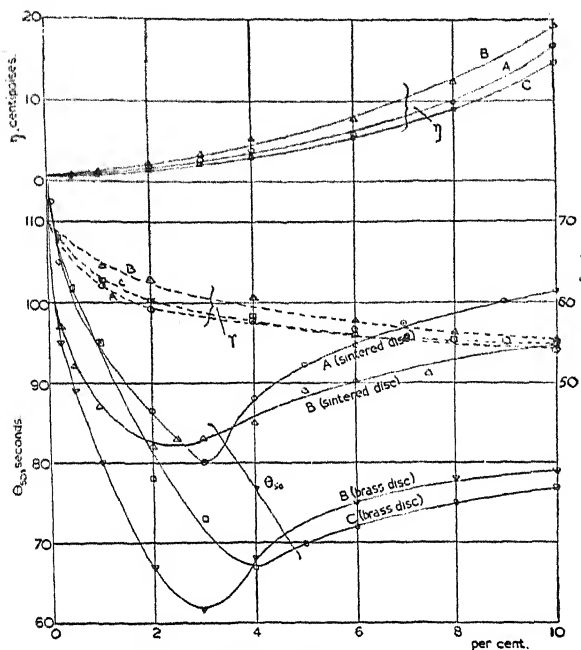


FIG. 5. GELATINS, 38°C.

pH 3 and 11. These results are given in Fig. 6.

The presence of capillary active impurities was suspected and was confirmed by de-ashing, when normal behaviour resulted in all concentrations (see also Fig. 6). In view of these experiments it seems probable that unsuspected impurities were responsible for certain contradictory statements made on the foaming of glues by Trotman and Hack-

ford,^{5(a)} who found that sodium hydroxide increased its foaming power and hydrochloric acid caused a decrease; and by Watson,^{5(b)} who found that both acid and alkali increased foaming.

The foaming of gelatin has largely been attributed to impurities, particularly peptones,¹⁶ and indeed it has been suggested that solutions of pure gelatin do not foam. This, however, has yet to be substantiated practically. But that this may be so receives some confirmation from the fact that of the normal gelatins investigated maximum foam did not occur at pH 4.7, but just above it, even with the de-ashed sample. This would imply

that either the three gelatins have an unusually high isoelectric point, or the adsorbed layer from which the foaming characteristics are de-

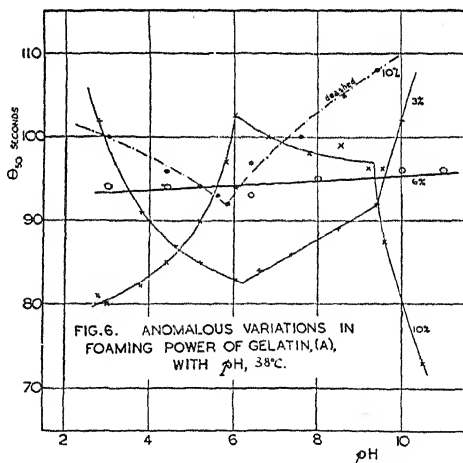


FIG. 6. ANOMALOUS VARIATIONS IN FOAMING POWER OF GELATIN, (A), WITH pH, 38°C.

¹⁶ Cf. Bancroft, *Applied Colloid Chemistry*, 1932, New York, p. 374.

rived does not consist of plain gelatin but contains some foreign substance tending to raise the isoelectric point. Further evidence of this latter possibility is given by the effect of 0.5 % ovalbumen on the foaming power of gelatin C in 10 % solution, when little change in θ_{50} occurred between pH 3 and 11, the curve resembling that of 0.5 % ovalbumen alone. It thus appears that ovalbumen is preferentially adsorbed, and that the foaming characteristics are derived from this adsorbed layer and not from the gelatin *per se*. Recently E.C.E. Hunter¹⁷ has observed that small quantities of casein profoundly modify the surface and foaming properties of gelatin solutions.

Summary.

A comparison of the main methods of studying foam formation and stability has been made, and details of a modification of the "porous septum" method reproducible to 3.5 % are given.

Solutions of saponins, alkyl sodium sulphates, sodium oleate, commercial wetting agents and gelatins have been studied by this method, and the following conclusions have been reached:

1. With most substances there is an optimum foam concentration.
2. In some cases this optimum occurs where surface tension is changing rapidly with concentration.
3. As with emulsions,¹⁸ it is not low surface tension *per se* that ensures stability, but the nature of the adsorbed layer giving rise to the lowering of surface tension.
4. For the formation of a stable foam a certain amount of cohesion of the adsorbed layer is necessary, loss of cohesion resulting in a deterioration of foaming power. This occurs when the molecules of the film have more than one hydrophilic group in such positions as to permit anchorage flat in the surface.
5. With naturally occurring substances such as saponins and gelatins, foaming properties and surface tension may vary within wide limits, depending on the source.
6. Small amounts of capillary active impurities can profoundly modify the foaming properties of gelatin solutions particularly with respect to pH, *e.g.* ovalbumen appears to be preferentially adsorbed at the surface of solutions of gelatin to the almost complete exclusion of the latter.

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¹⁷ Hunter, 1941, *private communication*.

¹⁸ Cf. King, *Trans. Faraday Soc.*, 1941, **37**, 172.

PROPAGATION OF TEMPERATURE CHANGES THROUGH TEXTILES IN HUMID ATMOSPHERES. PART IV. EXTENDED THEORY OF TEMPERATURE PROPAGATION THROUGH TEXTILES.

BY H. E. DANIELS.

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1. In part II of the present series,¹ Cassie discusses the theory of heat and water vapour exchange when air flows through textiles under a given pressure difference, and the agreement with experiment is demonstrated in part III¹ by Cassie and Baxter. As the speed of air flow was in the experimental work of the order of 1.4 cm. per sec., the effect of diffusion of both heat and water vapour was tentatively considered to be negligible in comparison with the rate of transport in the air current. A simplified theory was worked out on this basis in part II, which showed that sudden changes of temperature or water vapour were propagated in two distinct wave fronts with speeds $u_1 = 5.7 \times 10^{-4}$ cm. per sec., and $u_2 = 1.4 \times 10^{-2}$ cm. per sec. for the wool and the air speeds chosen. Experiment showed that the slow wave front was not a sharply-defined discontinuity but was considerably smoothed out, and it was suggested in explanation that the non-homogeneous packing of the material gave rise to pores of varying cross-section through which the air could advance with different speeds.

In the present paper we show that, owing to the slowness of u_1 , the effect of diffusion cannot be ignored and also that if circulation is not maintained in the incident air, there is an appreciable lag due to diffusion back into the air. When these facts are taken into account, the shape of the curve is adequately explained.

2. Equations of Temperature and Water Vapour Change.

Consider a mass of textile through which air is moving bodily, and in which diffusion of heat and water vapour is taking place. The rate of air flow v at a point of the textile is a vector defined as the average volume of air per second per unit area of textile which crosses a small area at that point. It should not be confused with the average rate of flow in the pores, which exceeds v in the ratio of total volume of textile to available pore space. The water vapour concentration C is the average concentration of water vapour in the pores surrounding the point considered. The temperature T is unambiguous.*

We make the assumption that the density of the air remains constant, and that the various constants are unaffected by the change in

¹ Parts I, II and III, Cassie, King, Baxter, *Trans. Faraday Soc.*, 1940, **36**, 445.

* Henry² discusses the various possible definitions exhaustively. In his language, C is the "active" concentration and v the "overall" rate of flow under conditions of no absorption.

² Henry, *Proc. Roy. Soc., A*, 1939, **171**, 215.

water vapour by transport through the prism tends to zero with ϵ . The balance of heat and water vapour require that

$$\rho_a c_a dA \left[-\mathfrak{D}_1'' \left(\frac{\partial T}{\partial n} \right)_1 + \mathfrak{D}_2'' \left(\frac{\partial T}{\partial n} \right)_2 \right] = \epsilon dA \left(S_1 \frac{\partial T}{\partial t} + S_2 \frac{\partial T}{\partial t} - q_1 \rho_1 \frac{\partial M_1}{\partial t} - q_2 \rho_2 \frac{\partial M}{\partial t} \right)$$

$$\text{and } dA \left[-D_1'' \left(\frac{\partial C}{\partial n} \right)_1 + D_2'' \left(\frac{\partial C}{\partial n} \right)_2 \right] = \epsilon dA \left(2 \frac{\partial C}{\partial t} + \rho_1 \frac{\partial M_1}{\partial t} + \rho_2 \frac{\partial M_2}{\partial t} \right)$$

where $\partial/\partial n$ denotes differentiation along the normal from medium 1 to 2. Make ϵ vanishingly small, and we obtain the boundary conditions

$$\left. \begin{aligned} \mathfrak{D}_1'' \left(\frac{\partial T}{\partial n} \right)_1 &= \mathfrak{D}_2'' \left(\frac{\partial T}{\partial n} \right)_2 \\ D_1'' \left(\frac{\partial C}{\partial n} \right)_1 &= D_2'' \left(\frac{\partial C}{\partial n} \right)_2 \end{aligned} \right\} \quad (3)$$

and

$$T_1 = T_2, \quad C_1 = C_2.$$

4. Simplifying Assumption.

In the case of diffusion alone, considered by Henry,² where $v = 0$, and also when diffusion is neglected as in part II, it was possible to discover functions of the form $f = rT + sC$ such that f_1 and f_2 satisfy independent equations. For the pair of equations (2) this is not in general possible. It happens, however, that \mathfrak{D}'' and D'' are numerically of the same order at low packing densities of the order of 0.2 g./cm.³. For example, in air the accepted values are $\mathfrak{D}'' = 0.19$, $D'' = 0.24$, while at a packing density of 0.2 g./cm.³ the results of Speakman and Chamberlain⁴ give approximately $K = 70 \times 10^{-6}$. Taking $\rho_a = 1.2 \times 10^{-3}$ g./cm.³ and $c_a = 0.24$ cal./°C. it is found that $\mathfrak{D}'' = 0.24$. Henry gives $D'' = 0.22$ at $\rho = 0.2$ for cotton, and the figure for wool should be almost the same.

The assumption that $\mathfrak{D}'' = D''$ makes it again possible to discover functions f satisfying independent equations, and the analysis is thereby considerably simplified. In a later section we indicate how the results may subsequently be adjusted in a simple manner to allow for a small discrepancy between \mathfrak{D}'' and D'' . Consequently we replace \mathfrak{D}'' and D'' by

$$\mu = \frac{1}{2}(\mathfrak{D}'' + D'')$$

and equations (2) become

$$\left. \begin{aligned} \frac{\mu}{\mathfrak{D}} \left(\alpha \frac{\partial C}{\partial t} - \frac{\partial T}{\partial t} \right) &= v \text{ grad } T - \mu \nabla^2 T, \\ \frac{\mu}{D} \left(\beta \frac{\partial T}{\partial t} - \frac{\partial C}{\partial t} \right) &= v \text{ grad } C - \mu \nabla^2 C. \end{aligned} \right\} \quad (2a)$$

Functions of the form $* f = rT + sC$ are independent if

$$\frac{1}{r} \left(\frac{r}{\mathfrak{D}} - \frac{s\beta}{D} \right) = \frac{1}{s} \left(\frac{s}{D} - \frac{r\alpha}{\mathfrak{D}} \right) = \frac{1}{\gamma} \quad (4)$$

⁴ Speakman and Chamberlain, *J. Text. Inst.*, 1930, 21, T 29.

* The notation $f = rT + sC$ accords with that of part II. Henry² uses $f = rC + sT$.

and (2a) are equivalent to

$$\mu \nabla^2 f - v \operatorname{grad} f = \frac{\mu}{\gamma} \frac{\partial f}{\partial t} \quad (5)$$

where $f = f_1, f_2$ correspond to the roots γ_1, γ_2 , of

$$\left(\frac{1}{\gamma} - \frac{1}{\mathfrak{D}}\right)\left(\frac{1}{\gamma} - \frac{1}{D}\right) = \frac{\alpha\beta}{D\mathfrak{D}} \quad (6)$$

Equation (5) may also be conveniently written

$$\gamma \nabla^2 f - u \operatorname{grad} f = \frac{\partial f}{\partial t}$$

where *

$$u = \frac{\gamma v}{\mu}$$

The values of r and s are determined from (4) on substituting the values of γ_1 and γ_2 , and using the appropriate conditions of the problem. In the case where T and C ultimately attain final values, T_0 and C_0 , throughout the textile it may be taken for convenience that f_1 and f_2 both attain the value $f = 1$ and from (4) and (6) after some reduction it is found that

$$\left. \begin{aligned} T &= T_0 \frac{\left[\left(\frac{1}{D} - \frac{1}{\gamma_1}\right)f_1 - \left(\frac{1}{D} - \frac{1}{\gamma_2}\right)f_2\right]}{\left(\frac{1}{\gamma_2} - \frac{1}{\gamma_1}\right)} + C_0 \frac{\frac{\alpha}{\mathfrak{D}}(f_1 - f_2)}{\left(\frac{1}{\gamma_2} - \frac{1}{\gamma_1}\right)} \\ C &= T_0 \frac{\beta}{D} \frac{(f_1 - f_2)}{\left(\frac{1}{\gamma_2} - \frac{1}{\gamma_1}\right)} + C_0 \frac{\left[\left(\frac{1}{\mathfrak{D}} - \frac{1}{\gamma_1}\right)f_1 - \left(\frac{1}{\mathfrak{D}} - \frac{1}{\gamma_2}\right)f_2\right]}{\left(\frac{1}{\gamma_2} - \frac{1}{\gamma_1}\right)} \end{aligned} \right\} \quad (7)$$

These formulæ are exactly equivalent to (13), (14) of part II.

In the external air we have :

$$\mathfrak{D}_a'' \nabla^2 T - v \operatorname{grad} T = \frac{\partial T}{\partial t},$$

$$D_a'' \nabla^2 C - v \operatorname{grad} C = \frac{\partial C}{\partial t}.$$

As before, we replace \mathfrak{D}_a'' and D_a'' by $\mu_a = \frac{1}{2}(\mathfrak{D}_a'' + D_a'')$ and the appropriate adjustment can be subsequently made as described in section 9. It is found below, however, that the solutions are to the first order independent of μ/μ_a so the assumption is not in any case important. Consequently we may write

$$\mu_a \nabla^2 f_a - v \operatorname{grad} f_a = \frac{\partial f_a}{\partial t} \quad (8)$$

where $f_a = rT + sC$ externally, and at the air-textile boundary,

$$f_a = f, \quad \mu_a \frac{\partial f_a}{\partial n} = \mu \frac{\partial f}{\partial n} \quad (9)$$

* It was considered better in the present paper to develop the formulæ in terms of the scalar quantities \mathfrak{D} , D and γ , rather than in terms of V , W and u as defined in part II. The relation between them is $V/\mathfrak{D} = W/D = u/\gamma = v/u$.

5. Solution of the Equations.

In practice, conditions at an air-textile interface will usually lie somewhere between the following two extremes:—

(a) A vigorous circulation maintained in the external air, which is then effectively a reservoir of T and C .

(b) Circulation absent, in which case diffusion into the external air becomes important. For brevity we refer to this process as "back diffusion."

Solutions of the equations will now be obtained in cases (a) and (b) for the rise in T and C at a point in the textile, when T and C in the external air are suddenly increased to T_0 and C_0 , T and C being initially zero throughout both air and textile. In terms of the functions $f = rT + sC$ the conditions are:

$$\begin{aligned} f_a &= 0, & f &= 0, & t &< 0 \\ f_a &= 1, & f &= 0, & t &= 0, \end{aligned}$$

6. Method of Solution.

The Heaviside-Laplace method of solving the equations is used. The Laplace transform of $f(x, t)$,

$$F(x, p) = p \int_0^\infty f(x, t) e^{-pt} dt$$

satisfies an ordinary differential equation in x obtained by writing p for $\frac{\partial}{\partial t}$ and $F - f(x, 0)$ for f in the original equation. Its solution, subject to the boundary conditions, is then transformed into the appropriate solution for $f(x, t)$ by means of the inverse transform:

$$f(x, t) = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} F(x, p) e^{pt} \frac{dp}{p}, \quad a > 0.$$

The initial conditions are automatically taken care of by this method. The direct evaluation of the contour integral is usually avoided by expressing $F(x, p)$ in terms of functions whose transform is known. For example, the expansion of $F(x, p)$ in inverse powers of p gives $f(x, t)$ on replacing $\frac{1}{p^n}$ by $\frac{t^n}{n!}$. The method is fully described by Jeffreys⁵ and many examples on heat conduction are worked out in Chapter V of his book. A rather different treatment is given by Carson.⁶ The details of the inverse transformation are, therefore, not given here. It should be noted that $F(x, \infty) = f(x, 0)$ and $F(x, 0) = f(x, \infty)$.

7. One Dimension.

For a one dimensional air-textile system,

$$v_x = v, \quad v_y = v_z = 0.$$

From (1), $v = \text{constant}$, and the equations are

$$\left. \begin{aligned} \mu_a \frac{\partial^2 f_a}{\partial x^2} - v \frac{\partial f_a}{\partial x} &= \frac{\partial f_a}{\partial t} \\ \gamma \frac{\partial^2 f}{\partial x^2} - u \frac{\partial f}{\partial x} &= \frac{\partial f}{\partial t} \end{aligned} \right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

⁵ H. Jeffreys, *Operational Methods in Math. Physics*, 2nd ed., Camb. Univ. Press.

⁶ J. R. Carson, *Electric Circuit Theory and Operational Calculus* (McGraw-Hill).

The simplest case to consider is when the textile extends from $x = 0$ to ∞ . Closed expressions are obtained with both sets of boundary conditions (a) and (b) which enable the magnitude of the "back diffusion" effect to be estimated.

(a) *Surface kept at T_0, C_0 .*—For all $t > 0$, $f(0, t) = 1$. The transformed equation is

$$\gamma \frac{\partial^2 F}{\partial x^2} - u \frac{\partial F}{\partial x} = pF,$$

where $F(0, p) = 1$. Write $h = \frac{u}{\gamma} = \frac{v}{\mu}$.

The appropriate solution is:

$$F = e^{\frac{hx}{2}} \left[1 - \sqrt{1 + \frac{4p}{hu}} \right].$$

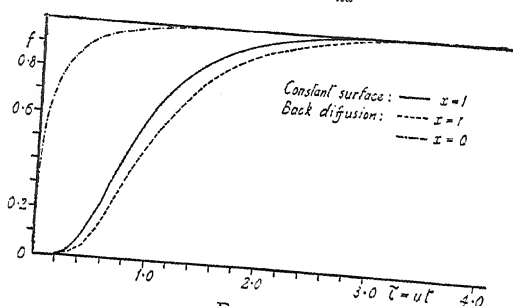


FIG. 1.

This transforms back to

$$f = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{x - ut}{2} \sqrt{\frac{h}{ut}} \right) + e^{hx} \operatorname{erfc} \left(\frac{x + ut}{2} \sqrt{\frac{h}{ut}} \right) \right] \quad (11)$$

where

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-y^2} dy.$$

Fig. 1 shows f plotted against $\tau = ut$, x being taken as 1 cm. and

$$h = \frac{v}{\mu} = \frac{1.4}{0.22} = 6.36.$$

The f curve may be compared with the upper part of the experimental curve B given in part III, p. 460, reproduced in Fig. 2. There is agreement in general shape, but at $t = 30$ min. which corresponds to $\tau = 1$, the latter has attained 50 % of the rise above the first equilibrium, whereas in Fig. 1, $\tau = 1$ corresponds to a rise of 60 %. Since in the experimental set-up there was no textile beyond the point at which temperature was measured, an even greater rise would be expected in the experiment at $t = 30$ min. The discrepancy indicates that T and C did not rise instantaneously to T_0, C_0 at the surface, and we now consider the effect of diffusion back into the air in slowing down the advance of the disturbance.

(b) *Case of Back Diffusion.*—The transformed equations are:—

$$\left. \begin{aligned} \mu_a \frac{\partial^2 F_a}{\partial x^2} - v \frac{\partial F_a}{\partial x} &= p(F_a - 1) \\ \gamma \frac{\partial^2 F}{\partial x^2} - u \frac{\partial F}{\partial x} &= pF \end{aligned} \right\} \quad (12)$$

The boundary conditions to be satisfied are $F_a = F \frac{\partial F_a}{\partial x} = \theta \frac{\partial F}{\partial x}$ at $x = 0$, where $\theta = \mu/\mu_a$, and the appropriate solutions are :

$$F_a = 1 - \frac{\left(\sqrt{1 + \frac{4p}{hu}} - 1\right)e^{\frac{\theta hx}{2}\left[1 + \sqrt{1 + \frac{4p}{\theta hu}}\right]}}{\left(\sqrt{1 + \frac{4p}{\theta hv}} + \sqrt{1 + \frac{4p}{hu}}\right)}$$

$$F = \frac{\left(1 + \sqrt{1 + \frac{4p}{\theta hu}}\right)e^{\frac{hx}{2}\left[1 - \sqrt{1 + \frac{4p}{hu}}\right]}}{\left(\sqrt{1 + \frac{4p}{\theta hv}} + \sqrt{1 + \frac{4p}{hu}}\right)}.$$

The exact evaluation of the inverse transforms of F_a and F is somewhat troublesome, but the following approximate procedure is quite adequate.

Inside the textile ($x > 0$).—The differential equation suggests that the disturbance is propagated with a speed of the order of u , and we expect that ut , and consequently p/u , is of unit order in the important part of the curve. Also the ratio $\lambda = u/v$ is very small for both u_1 and u_2 . The expression for F may, therefore, be written :

$$F = \frac{\left(1 + \sqrt{1 + \frac{4p}{\theta hu}} \cdot \lambda\right)e^{\frac{hx}{2}\left[1 - \sqrt{1 + \frac{4p}{hu}}\right]}}{\left(\sqrt{1 + \frac{4p\lambda}{\theta hu}} + \sqrt{1 + \frac{4p}{hu}}\right)}$$

and the expansion in powers of λ will yield a solution of asymptotic type, which is of value when ut/λ is large. The values of u quoted in part III, p. 460, are $u_1 = 5.7 \times 10^{-4}$, $u_2 = 1.4 \times 10^{-2}$, which lead to $\lambda_1 = 4.07 \times 10^{-4}$, $\lambda_2 = 10^{-2}$, taking $v = 1.4$ cm./sec. The value of λ_1 is so small that, in fact, over the whole useful range of t , we need only consider the term independent of λ . In the case of λ_2 , the contribution of the term in λ may be appreciable, but it is not important in view of the relatively short time taken to reach the first equilibrium level. So to this order of approximation it is sufficient to take :

$$F \sim \frac{2e^{\frac{hx}{2}\left(1 - \sqrt{1 + \frac{4p}{hu}}\right)}}{\left(1 + \sqrt{1 + \frac{4p}{hu}}\right)}$$

$$= -u \frac{\partial}{\partial x} \cdot \frac{1}{p} e^{\frac{hx}{2}\left(1 - \sqrt{1 + \frac{4p}{hu}}\right)}$$

and from the previous solution we obtain immediately :

$$f \sim -u \frac{\partial}{\partial x} \int_0^t dt \cdot \frac{1}{2} \left\{ \operatorname{erfc} \left(\frac{x - ut}{2} \sqrt{\frac{h}{ut}} \right) + e^{hx} \operatorname{erfc} \left(\frac{x + ut}{2} \sqrt{\frac{h}{ut}} \right) \right\}$$

which reduces to the more convenient form,

$$f \sim \frac{1}{2} \operatorname{erfc} \left(\frac{x - ut}{2} \sqrt{\frac{h}{ut}} \right) + \sqrt{\frac{hut}{\pi}} \cdot e^{-\frac{h(x-ut)^2}{4ut}}$$

$$- e^{hx} [1 + (x + ut)h] \cdot \frac{1}{2} \operatorname{erfc} \left(\frac{x + ut}{2} \sqrt{\frac{h}{ut}} \right). \quad (13)$$

Note that to the order of approximation being considered the curves for f_1 and f_2 again depend only on h and ut and not on θ , and their shape is independent of u (or γ).

The dotted curve, Fig. 1, shows f plotted against $\tau = ut$, with $x = 1$, $h = 6.36$, and the effect of back diffusion in slowing the advance of the disturbance is evident. At $\tau = 1$ the rise is now only 48 %.

At the interface ($x = 0$).—Setting $x = 0$ in the formula gives :

$$f(0, t) \sim 1 - (1 + \frac{1}{2}hut) \operatorname{erfc} \frac{1}{2}\sqrt{hut} + \sqrt{\frac{hut}{\pi}} e^{-\frac{hut}{4}}$$

for the behaviour at the surface of the textile. It is also plotted on Fig. 1. The formula is not valid for small ut , but on making $p \rightarrow \infty$ in $F(0, p)$ it is found that, when $t = 0$,

$$f(0, 0) = F(0, \infty) = \frac{\sqrt{\lambda}}{(\sqrt{\lambda} + \sqrt{\theta})}.$$

In the outside air ($x < 0$).—At $x = -y$ we have :

$$F_a = 1 - \frac{\left(\sqrt{1 + \frac{4p}{hu}} - 1\right) e^{-\frac{\theta hy}{2}} \left(1 + \sqrt{1 + \frac{4p\lambda}{\theta hu}}\right)}{\left(\sqrt{1 + \frac{4p}{\theta hu}} \lambda + \sqrt{1 + \frac{4p}{hu}}\right)}$$

so that except for small values of ut we may write :

$$F_a \sim 1 - \frac{\left(\sqrt{1 + \frac{4p}{hu}} - 1\right) e^{-\theta hy}}{\left(\sqrt{1 + \frac{4p}{hu}} + 1\right)}$$

i.e.

$$1 - F_a \sim \left[1 - \frac{2}{\left(\sqrt{1 + \frac{4p}{hu}} + 1\right)}\right] e^{-\theta hy}.$$

Comparison with the previous result shows that :

$$1 - f(-y, t) \sim [1 - f(0, t)] e^{-\theta hy}$$

so that $f(-y, t)$ increases with t to $f = 1$, if t is not too small. But the initial value of $f(-y, t)$ is also 1, as can be seen on making $p \rightarrow \infty$ in the exact expression for f_a . At a point at distance y from the surface of the textile, therefore, the value of f drops from $f = 1$ to a lower value, and rises more slowly back to $f = 1$ in a manner similar to the behaviour of f at the surface. A more exact treatment indicates that the initial drop from $f = 1$ is somewhat rounded off as y increases, but for any value of y , f will never fall below $[1 - f(0, 0)] e^{-\theta hy} < e^{-\theta hy}$. In the experiments $h = 6.36$ and $\theta = 0.92$, so the disturbance should be inappreciable at distances $y > 1$ cm.

8. Case of Diffusion Alone.

It seems worth noting here that although the back diffusion effect is fairly small with air speeds of the order considered, it can be shown that the effect is by no means small in the case of diffusion alone, when $v = 0$, and in fact the two types of surface condition may then lead to rates of diffusion of an entirely different order of magnitude. On the other hand, condition (b) would be almost impossible to maintain outside a large mass of textile when $v = 0$, as diffusion would operate in the air at a considerable distance from the surface, and convection and other air disturbances

would intervene. In some rooms used for conditioning textiles, however, the state of the atmosphere is probably nearer (b) than (a), and the results given by Henry² for surface condition (a) then require correcting for the slow change at the surface, as indicated in § 9 of his paper.

9. Adjustment when $\mathfrak{D}'' \neq D''$.

We return to equation (2) and consider the error introduced by the assumption that $\mathfrak{D}'' = D''$. Suppose now that they differ by a small quantity

$$2\epsilon = \mathfrak{D}'' - D''.$$

Re-writing equations (2) in the form

$$\nabla^2 T + \frac{1}{\mathfrak{D}} \left(\alpha \frac{\partial C}{\partial t} - \frac{\partial T}{\partial t} \right) = \frac{v}{(\mu - \epsilon)} \text{grad } T$$

$$\nabla^2 C + \frac{1}{D} \left(\beta \frac{\partial T}{\partial t} - \frac{\partial C}{\partial t} \right) = \frac{v}{(\mu + \epsilon)} \text{grad } C$$

they may be combined, using the previous values of r and s , to give

$$\begin{aligned} \nabla^2 f_1 - \frac{1}{\gamma_1} \frac{\partial f_1}{\partial t} &= v \text{grad} \left(\frac{r_1}{\mu - \epsilon} T + \frac{s_1}{\mu + \epsilon} C \right) \\ \nabla^2 f_2 - \frac{1}{\gamma_2} \frac{\partial f_2}{\partial t} &= v \text{grad} \left(\frac{r_2}{\mu - \epsilon} T + \frac{s_2}{\mu + \epsilon} C \right). \end{aligned}$$

These are readily manipulated into the form

$$\left. \begin{aligned} \nabla^2 f_1 - \left(\frac{\mu - a\epsilon}{\mu^2 - \epsilon^2} \right) v \text{grad } f_1 - \frac{1}{\gamma_1} \frac{\partial f_1}{\partial t} &= \frac{2\epsilon b_1}{(\mu^2 - \epsilon^2)} v \text{grad } f_2 \\ \nabla^2 f_2 - \left(\frac{\mu + a\epsilon}{\mu^2 - \epsilon^2} \right) v \text{grad } f_2 - \frac{1}{\gamma_2} \frac{\partial f_2}{\partial t} &= \frac{2\epsilon b_2}{(\mu^2 - \epsilon^2)} v \text{grad } f_1 \end{aligned} \right\} \quad (14)$$

where $a = \frac{\left(\frac{1}{\mathfrak{D}} - \frac{1}{D} \right)}{\left(\frac{1}{\gamma_2} - \frac{1}{\gamma_1} \right)}$, and in the case which concerns us when $C_0 = 0$,

$$b_1 = \frac{\left(\frac{1}{\gamma_2} - \frac{1}{D} \right)}{\left(\frac{1}{\gamma_2} - \frac{1}{\gamma_1} \right)}, \quad b_2 = \frac{\left(\frac{1}{\gamma_2} - \frac{1}{\mathfrak{D}} \right)}{\left(\frac{1}{\gamma_2} - \frac{1}{\gamma_1} \right)}.$$

When ϵ was assumed to be zero, the two components f_1 and f_2 turned out to be so widely separated on the time scale that there was a distinct section of the T curve (C, Fig. 2) over which f_1 had to all intents attained its full value $f_1 = 1$ before f_2 had perceptibly risen from $f_2 = 0$. It may be safely assumed, therefore, that under these conditions the value of f_2 is constant over the important range of t for f_1 , and vice versa. Moreover, the same state of affairs will hold for a slight change in position of the point of measurement, so that we may take $\text{grad } f_2 = 0$, $\text{grad } f_1 = 0$ on the right hand side of equations (14).

To the first order, therefore, the effect of the discrepancy ϵ is simply to decrease u_1 and to increase u_2 by a fraction $\epsilon a / \mu$. The new curves so obtained may then be checked to see that the condition $\text{grad } f = 0$, necessary for the approximation, still holds over the required ranges.

It was found for the experiments of part III that the correction was less than 2 %.

10. Comparison with Experiment.

The experimental curves represent the change in temperature at the inner surface of a hollow cylinder when the temperature of the air outside the cylinder is suddenly increased, the volume rate of flow of air into the cylinder being maintained constant. The curve obtained above for the case of linear flow into a semi-infinite mass of textile was used to construct the theoretical curve *C* of Fig. 2, for comparison with curve B, part III, which is also reproduced. They are so similar that we may reasonably assume the general shape of the experimental curves to be adequately explained. For complete agreement it is necessary to solve the equations for the case of a hollow cylinder, in which case the computation of *f*, though straightforward, is laborious.

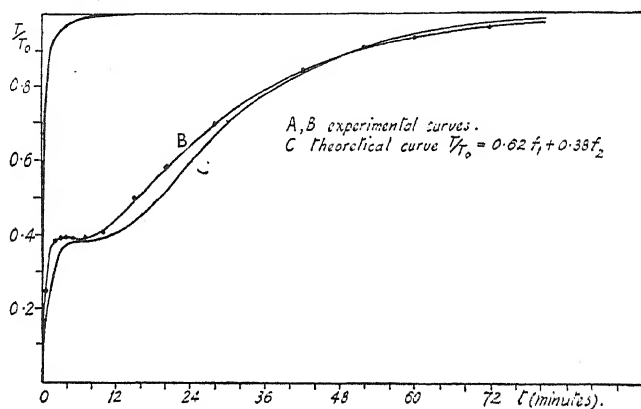


FIG. 2.

It is useful, however, to have a method of estimating u_1 and u_2 from the curves without having to compute *f* in detail, and this may be most conveniently done in the following way:—

11. Estimation of *u* by Areas.

$$\text{Let} \quad F(p) = p \int_0^{\infty} f(t) e^{-pt} dt$$

and suppose that $f(t) \rightarrow 1$ as $t \rightarrow \infty$.

$$\text{Then} \quad 1 - F(p) = p \int_0^{\infty} [1 - f(t)] e^{-pt} dt$$

$$\text{and hence} \quad -F'(0) = \int_0^{\infty} [1 - f(t)] dt \quad (15)$$

provided the integral exists. We thus have a convenient expression for the area between the curve and its asymptote, or, what is the same thing, for the distance \bar{t} of the centre of gravity of this area from $t = 0$, which we expect to be of the order of x/u .

For example, with the surface at constant T_0 , C_0 we had for the semi-infinite case:

$$F(p) = e^{\frac{hx}{2}} \left(1 - \sqrt{1 + \frac{4p}{hu}} \right)$$

from which $\bar{t} = -F'(0) = x/u$ exactly. On the other hand, when there is back diffusion it is found that $\bar{t} = \frac{I}{u} \cdot (x + \frac{I}{h})$. In more complicated cases it is not necessary to find $F(p)$ explicitly, since $\frac{d}{dx}F'(0)$ satisfies a first order differential equation which is easily solved. For example, from (12) since $F(0) = F_a(0) = 1$,

$$\mu_a \frac{d^2 F'_a(0)}{dx^2} - v \frac{dF'_a(0)}{dx} = 0$$

and

$$\gamma \frac{d^2 F'(0)}{dx^2} - u \frac{dF'(0)}{dx} = 1 \text{ in the textile.}$$

The solutions

$$F'_a(0) = Ae^{\theta h x}; F'(0) = -\frac{x}{u} - \frac{I}{hu} + \left(A + \frac{I}{hu}\right)e^{hx}$$

satisfy the conditions $F'_a(0) = F'(0)$ at $x = 0$, and $F'_a(0) = 0$ at $x = -\infty$. If the textile extends to $x = l$ and turbulence is maintained in the issuing air, the conditions $\frac{dF'(0)}{dx} = 0$ at $x = l$ also holds. So for a slab of thickness l ,

$$\bar{t} = \frac{x}{u} + \frac{I}{hu} - \frac{I}{hu} e^{h(x-l)}$$

and at $x = l$, $\bar{t} = l/u$ exactly, *when there is back diffusion*. As was to be expected, the removal of textile beyond $x = l$ has speeded up the rate of change at that point.

With the surface kept at T_0, C_0 , the condition at $x = 0$ is $F'(0) = 0$, so that

$$F'(0) = -\frac{x}{u} + \frac{I}{hu} (e^{h(x-l)} - e^{-hl})$$

leading to

$$\bar{t} = \frac{l}{u} - \frac{I}{hu} (1 - e^{-hl}).$$

With

$$l = 1, h = 6.36, \bar{t} = \frac{0.843}{u}.$$

TABLE I.—VALUES OF $u\bar{t}$ AT 1 CM. FROM THE INTERFACE.

	Constant Surface.	Back Diffusion.
Semi-infinite mass of textile $0 \leq x \leq \infty$	1.000	1.157
Infinite slab $0 \leq x \leq 1$	0.843	1.000
Cylinder $\frac{3}{8}'' \leq r \leq 1\frac{3}{8}''$	0.736	0.972

The equations for a cylindrical body can be solved in exactly similar fashion. The experiments of part III were performed on a hollow cylinder of radii $\frac{3}{8}''$, $1\frac{3}{8}''$ and $h = 6.36$, in which case the values of \bar{t}

are found to be $\bar{t} = \frac{0.972}{u}$ with back diffusion, and $\bar{t} = \frac{0.736}{u}$ with the surface kept at T_0, C_0 . These results are set out in Table I.

12. Correction for non-instantaneous initial change.

In practice it will be difficult to cause T and C to change instantaneously from 0 to T_0 , C_0 in the surrounding atmosphere even when no textile is present, and the curve A (part III, p. 460, reproduced in Fig. 2) in fact shows that the change required 10 minutes to be complete in that case, although the major part of the change had occurred within a few minutes. Suppose, therefore, that the condition of initial sudden change of f_a from 0 to 1 is replaced by a finite change in the incident air represented by $f_a = g(t)$, where $g(0) = 0$, $g(\infty) = 1$, and let the transform of $g(t)$ be $G(p)$. Then the effect on the solution for f is to alter its transform to

$$H(p) = G(p)F(p),$$

and since $F(0) = G(0) = 1$, it follows that $F'(0) = H'(0) - G'(0)$. But $-G'(0)$ is the area between the curve $g(t)$ and its asymptote. Consequently when the initial change is not sudden, but is represented by $g(t)$, then $-F'(0)$ gives the area contained between the curves $f(t)$ and $g(t)$.

Summary.

The theory of heat and water vapour transfer through textiles is given when both diffusion and air transport are considered, and the shape of the experimental curves obtained in part III is adequately explained. A method is given for estimating the speeds of the fast and slow components by areas without detailed fitting of the theoretical curves.

The author wishes to thank Dr. A. B. D. Cassie and Mr. S. Baxter for much essential discussion and advice, and Miss V. Farrow for performing the computations.

RATE OF PROPAGATION OF TEMPERATURE CHANGE THROUGH TEXTILES IN HUMID ATMOSPHERES. PART V. THE COMPARISON OF DIFFERENT TEXTILE FIBRES.

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In part III¹ of this series, curves showing the rate of propagation of temperature change through samples of cotton and wool were given. Those curves, which were compared with the theoretical results, were not obtained under identical experimental conditions, and accurate direct comparison of the behaviour of the two fibres was not possible. It is of interest, however, to have a knowledge of how different textile fibres behave with regard to heat properties, since, similar cloths may be made out of different fibres or blends of several fibres and it is of interest to be able to predict the resistance of the resultant fabrics to sudden temperature changes. To do this it is essential to know the speed with which a given temperature change is propagated through

¹ Parts I, II and III, Cassie, King, Baxter, *Trans. Faraday Soc.*, 1940, **36**, 445.

masses of the various textile fibres. In the present publication the rates of propagation of temperature change through cylinders of several different textile fibres under identical experimental conditions are compared. The results may be compared with theoretical values. The mean times used for comparison with the theoretical values are obtained from the experimentally determined curves using the method of areas given in part IV.

Experimental.

The experimental set-up was a revised version of the one used to obtain the results given in part III * and will only be briefly described here. Air at 20° C. and 60 % R.H. was blown through the textile sample until it was fully conditioned, the equilibrium conditions being approached in the direction of increasing regain. The temperature of the inflowing air was then suddenly changed to 35° C. and the same water vapour pressure maintained. The increase in temperature of the air after passing through the textile cylinder was recorded against time. The cylinders of the different textile fibres were made of identical size and density and the same air flow was used in every case. The curves obtained for the different textile fibres are therefore directly comparable. The results obtained are shown in Figs. 1a and 1b. The theory of part II suggests

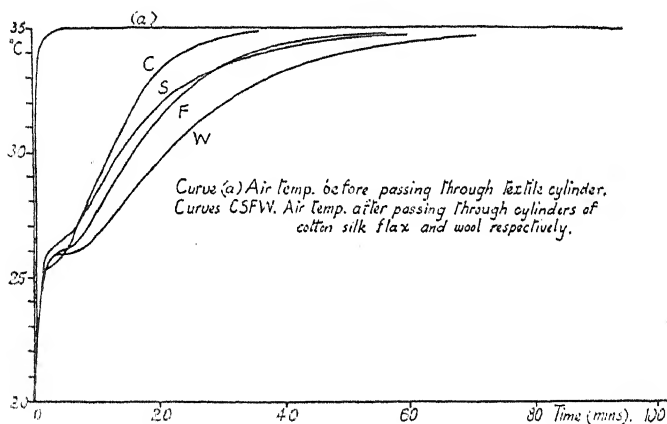


FIG. 1a.

that the temperature change should be propagated in two well defined wave fronts which traverse the sample at different velocities. This theory neglected the effects of diffusion and when diffusion effects are taken into consideration it is seen in part IV that the shape of the experimental curves can be well explained. It is of interest, however, to compare the average time of propagation of the temperature wave through the textile cylinder deduced using the method of areas given in part IV with the time deduced theoretically. This is done later.

Numerical Calculations.

By considering an air-water vapour mixture flowing through a semi-infinite slab of textile fibres in equilibrium with the temperature and

* Fig 2, p. 459 of part III. should show the bottom of the textile cylinder BC to be closed.

water vapour concentration of the air, and the changes which take place when the temperature and water vapour concentration of the inflowing air are suddenly changed, it has been shown that two linear functions of concentration and temperature are propagated in unchanged form through the textile fibres. These two functions f_1 and f_2 are propagated with velocities u_1 and u_2 through the fibres. The velocities are given by the equation.*

$$\left(\frac{1}{u} - \frac{1}{v} \times \frac{1}{u} - \frac{1}{w} \right) = \frac{\alpha\beta}{vw}$$

where

$$V = \frac{v}{(S + q\rho\omega)\rho_a c_a} ; \quad \alpha = \frac{q\rho\sigma}{S + q\rho\omega}$$

$$W = \frac{v}{1 + \rho\sigma} ; \quad \beta = \frac{\rho\omega}{1 + \rho\sigma}$$

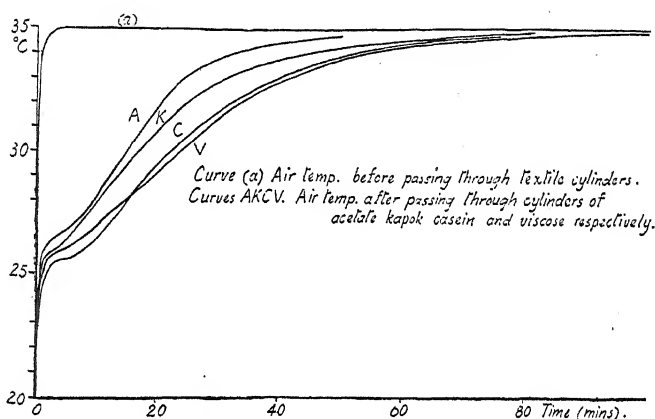


FIG. 1b.

and S = heat required to raise the temperature of 1 c.c. of the air-textile mixture through 1° C. assuming no water vapour exchange; ρ_a and c_a are the density and specific heat of air at constant pressure; q is the latent heat of absorption per gm. of water vapour absorbed by the textile; ρ is the overall density of the fibres and ω and σ are constants given by the equation²

$$\frac{\partial M}{\partial t} = \sigma \frac{\partial C}{\partial t} - \omega \frac{\partial T}{\partial t} \quad (2)$$

where M is the fractional regain of the fibres; C is the concentration of water vapour and T the temperature; σ is the fractional change in regain per unit change in concentration at constant temperature and ω = fractional change in regain per $^\circ$ C. change in temperature at constant concentration.

In the present work we are only concerned with a change in

* See footnote to part IV, p. 2.

² Henry, *Proc. Roy. Soc., A*, 1939, 171, 215.

temperature, and in this case the amplitudes of the wave fronts f_1 and f_2 are given by the equation

$$\Delta T = \Delta_0 T \frac{\left(\frac{1}{\bar{V}} - \frac{1}{u_2}\right)f_1 - \left(\frac{1}{\bar{V}} - \frac{1}{u_1}\right)f_2}{\left(\frac{1}{u_1} - \frac{1}{u_2}\right)} \quad (3)$$

the f_1 front being propagated with a velocity u_1 and the f_2 front with a velocity u_2 .

The present experimental results were obtained using the same density of fibres, the same air flow and the same temperatures and water vapour concentration in every case, and in working out the theoretical results, the only factors which vary with the fibres used are the values of specific heat, ω and σ . The variation of specific heat amongst the different textile fibres is extremely small, and an average value of 0.35 cal./g./°C. has been taken. This is quite justified since the value of the specific heat has little effect on the rate of propagation of the slower front, *i.e.*, the one of most interest for the present paper. We are now left with the variations of ω and σ which can be related as follows: when dM is zero equation (2) gives

$$\omega = \sigma \frac{dC}{dT} \quad (4)$$

and Kirchoffs' relation for constant regain is

$$\frac{1}{C} \frac{dC}{dT} = \frac{Q}{RT^2} - \frac{1}{T} \quad (5)$$

where Q is the latent heat of sorption per g. molecule of water vapour and R is the gas constant per g. molecule,

$$\text{i.e.} \quad \frac{1}{C} \frac{\omega}{\sigma} = \frac{Q}{RT^2} - \frac{1}{T} \quad (6)$$

By taking a constant value of Q and since the experimental conditions were the same in every case ω/σ is a constant and the only variable from sample to sample is the value of ω . It is justifiable to take Q as a constant since it is made up of two components; the latent heat of condensation of vapour to liquid, which is independent of the fibre, and a smaller component, the heat of wetting which depends on the fibre used. The latent heat of condensation may be taken as 560×18 cal./g. mol. at the temperature of the experiment and for the heat of wetting an average value of 90×18 cal./g. mol. has been used. Q cannot vary much for different textile fibres since the only variable is the heat of wetting which constitutes only a small fraction of Q . An equation connecting ω and u can, therefore, be obtained from equation (1) by substituting the values of the constants in the equation and rearranging. The values of the constants used in the experiments were as follows:

$$\begin{aligned} v &= 1.75 \text{ c.c./cm.}^2\text{/sec.} \\ \rho &= 0.147 \text{ g./c.c.} \\ \rho_a c_a &= 2.91 \times 10^{-4} \text{ cal./c.c./}^\circ\text{C.} \\ q &= 650 \text{ cal./g.} \\ \omega/\sigma &= 6.3 \times 10^{-7}. \end{aligned}$$

It is shown in part IV that for the case of an infinite slab of textile fibres of thickness l the distance t of the centre of gravity of the area between the experimental curves obtained for the temperature of the air before passing through the textile cylinder and the temperature of the air after passing through the textile cylinder should equal l/u exactly when there is back diffusion. For the case of the cylinder it has been shown that $\bar{t} = 0.972 \frac{l}{u}$ for the back diffusion case, provided that in the equations for u the velocity of the air is taken as the volume traversing unit area of the cylinder of radius $\frac{a+b}{2}$ where a and b are the inner and outer radii of the test sample.

In Fig. 2 the velocity of the f_1 front u_1 and the time t required for this front to traverse the sample are plotted against the corresponding values of ω . The values of u_2 are not given as they cannot be accurately

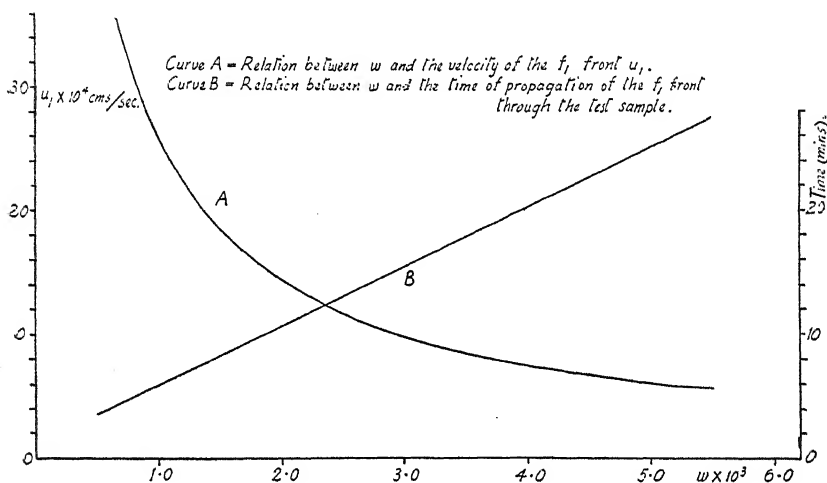


FIG. 2.

calculated: they depend on the difference between two large and nearly equal quantities and the calculations can therefore only give qualitative values.

Regain Curves.

It is seen from equation (1) that the theoretical velocity of the temperature wave through a given sample is a direct function of ω and, if ω is known, the velocity of the wave can be read off from Fig. 2, provided, of course, that the experimental conditions conform to those used in evaluating the equation. The fractional change in regain per $^{\circ}\text{C.}$ change in temperature at constant water vapour pressure, ω , can be obtained from the regain-relative humidity (R.H.) curve of the textile, since for a given change in temperature at constant water vapour pressure the change in R.H. can be calculated and the change in regain obtained from the regain-R.H. curve; ω is then found from the relation

$\omega = - \left(\frac{\Delta M}{\Delta T} \right)_p$. The value of ΔM found in this way is not strictly

accurate since it is deduced assuming that for constant R.H. the regain does not change with temperature. This is not strictly correct as at constant R.H. the regain decreases with increase of temperature. This fact would, if it was allowed for, give values of ω greater than those deduced using the above method and consequently would give a greater theoretical time for the propagation of the temperature change.

It is well known that for a given textile fibre the regain R.H. curve may vary quite considerably with the sample used especially with the artificial fibres, and it was decided to obtain the regain-R.H. curves for the textile samples actually used in determining the curves for the rate of propagation of temperature change. Mr. King of these laboratories very kindly undertook the determination of the regain-R.H. curves using a new experimental technique developed by him. In the present series of experiments the textile sample was conditioned to an R.H. of 60 % at 20° C. in the direction of increasing regain, and then the temperature of the inflowing air was suddenly raised to 35° C. keeping the water vapour pressure constant, *i.e.*, the R.H. of the air fell to 25 %. Thus an average value of ω is given by the difference in regain at 60 % R.H. and 25 % R.H. divided by the temperature difference of 15° C. The regains can be read off from the regain-R.H. curve using the drying half of the cycle.

The correction for the change in regain with temperature at constant R.H. cannot be made for all the textile fibres used since information on this point is lacking. The correction will be made in the case of cotton, wool and silk from the available information. The corrections are not accurate since the published data is far from consistent.

Results.

Only one result will be worked out in detail and the rest of the results tabulated.

Wool.—The change in fractional regain due to the change in R.H. from 60 % to 25 % caused by the increase of temperature from 20° C. to 35° C. is 0.066,

$$i.e. \quad \omega = \frac{0.066}{15} = 4.40 \times 10^{-3}/^{\circ}\text{C}.$$

The correction due to the temperature increase may be taken as an increase in ΔM equal to the decrease in regain caused by a temperature increase from 20° C. to 35° C. at a constant R.H. of 25 %. Values of this regain change obtained from published results are not in good agreement. Speakman and Cooper's³ results give 0.0062, Schloesing's⁴ results give 0.007, Hartshorn's⁵ results give 0.006 and Hedges's⁶ results give 0.0085. Taking a mean value of 0.0069 for this correction the corrected value of w becomes $4.86 \times 10^{-3}/^{\circ}\text{C}$. and from Fig. 2a the corresponding value of t is 24.4 min.

Since the temperature of the inflowing air does not change instantaneously, in order to find \bar{t} from the experimental curve it is necessary to integrate the area between the two curves (a) and (w) of Fig. 1a. Experimental difficulties prevent accurate determination of the curve (w) when the temperature difference between the inflowing and outflowing air is small, and so direct estimate of the area between the two curves is not accurate in the region of small temperature differences. The curve (w), however, takes up an exponential form for small values of temperature

³ Speakman and Cooper, *J. Text. Inst.*, 1936, **32**, T 191.

⁴ Schloesing, *Textile World Record*, Boston, 1908.

⁵ Hartshorn, *Trans. Am. Soc. Chem. Eng.*, 1918, **39**, 1073.

⁶ Hedges, *Trans. Faraday Soc.*, 1926, **22**, 178.

difference, since the solution of the differential equation is expressible as a Fourier-type expansion, whose coefficients are of the form $e^{-\Delta t}$ and for large t only the first term is important, and so it is possible to estimate the area between the two curves in the region where they become asymptotic by extrapolating the exponential.

Area between the curves (a) and (w) for—

$$\begin{aligned} t &< 40 \text{ min.} = 222.2; \\ t &> 40 \text{ min.} = 33.5 \text{ (estimated)}; \\ \therefore \bar{t} &= \frac{255.7}{9} = 28.4 \text{ min.} \end{aligned}$$

The amplitudes of the two fronts are obtained from equation (3). We get

$$\Delta T = \Delta_0 T (0.652 f_1 + 0.348 f_2).$$

For $\Delta_0 T = 15^\circ \text{C.}$ we have

and 5.2°C. associated with the faster wave,
 9.8°C. „ „ „ „ slower wave.

The experimental curve gives

and 5.9°C. associated with the faster wave,
 9.1°C. „ „ „ „ slower wave.

The results obtained using other textile fibres are tabulated in Tables I and II below:—

TABLE I.

Textile Fibre.	$\omega \times 10^3$.	Corrected Value of $\omega \times 10^3$.	Times of Propagation of the Slower Temp. Wave.	
			(min.) Theoretical.	(min.) Experimental.
Cotton . . .	3.06	3.39	15.7	13.8
Silk . . .	3.75		17.3	
			19.0	
Acetate . . .	3.14	4.37	22.0	19.8
Flax . . .	4.06		16.1	19.6
Kapok . . .	3.93		20.5	19.5
Wool . . .	4.40	4.86	19.9	23.6
			22.1	
Casein . . .	4.66		24.4	28.4
Viscose . . .	5.32		23.4	29.8
			26.6	30.0

TABLE II.

Textile Fibre.	Amplitude of Slower Wave.		Amplitude of Faster Wave.	
	Theoretical.	Experimental.	Theoretical.	Experimental.
	$^\circ\text{C.}$	$^\circ\text{C.}$	$^\circ\text{C.}$	$^\circ\text{C.}$
Cotton . . .	10.1	9.3	4.9	5.7
Silk . . .	10.0	8.6	5.0	6.4
Acetate . . .	10.1	8.5	4.9	6.5
Flax . . .	9.9	9.1	5.1	5.9
Kapok . . .	9.9	9.0	5.1	6.0
Wool . . .	9.8	9.1	5.2	5.9
Casein . . .	9.7	9.4	5.3	5.6
Viscose . . .	10.1	9.1	4.9	5.9

For the correction to ΔM due to the increase in temperature in the case of cotton a mean value of 0.005 has been taken. This average value has been obtained from the results of Urquhart and Williams⁷ which give 0.004, Schloesing's⁴ which give 0.008 and Hartshorn's⁶ which give 0.002. For the case of silk the correction to ΔM has been taken as 0.010, an average of the values obtained from the results of Schloesing⁴ 0.008, and Wilson and Fuwa⁸ 0.012. Qualitatively similar corrections will apply to the other textile fibres used.

Discussion of Results.

It has been clearly shown that a temperature change is transmitted through textile materials in two distinct wave fronts. The faster wave front traverses the sample in a time which is of the order of one minute. This is true for all the fibres examined as it depends largely on the specific heat which is roughly the same for all these fibres. The slower wave front traverses the sample in a time which depends on the value of ω and from Fig. 2 it is seen that the time is almost proportional to ω , where ω is a measure of the steepness of the regain R.H. curve of the textile and a textile with a steep regain-R.H. curve will have a greater resistance to propagation of temperature change than a textile with a less steep regain-R.H. curve. Thus from the clothing aspect, the steeper the regain-R.H. curve of the textile fibres used in the clothing the greater will be the resistance to temperature change when the wearer goes into a lower temperature with no change in water vapour pressure.

From Table I it is seen that there are considerable differences between the different fibres in the rate of propagation of temperature change. The textile fibres used can be roughly divided into two groups: those with a slow rate of propagation of temperature change *i.e.* kapok, wool, casein, and viscose, and those with a faster rate of propagation of temperature change, *i.e.*, cotton, silk, acetate and flax. The results obtained for silk, flax and wool may be taken as typical results for those fibres since there is little change in the regain-R.H. curves amongst different samples of the same type of fibre. The regains of these fibres vary little with the treatment they receive. In the case of cotton, however, the regain may vary through quite considerable limits according to the wet treatments received by the fibres, *e.g.*, the regain curves for scoured and mercerised cotton⁹ give values of $\omega = 2.0 \times 10^{-3}$ and 3.7×10^{-3} respectively. The curves for the synthetic fibres acetate and viscose rayon cannot be taken as typical for those fibres since the regain-R.H. curves vary quite considerably with different samples of the fibre, *e.g.*, for acetate rayon using the regains published in the *Rayon and Synthetic Yarn Handbook* and International Critical Tables the values of ω are 2.0 and 1.0×10^{-3} respectively: the sample of acetate rayon used in this work gives $\omega = 3.14 \times 10^{-3}$. For viscose rayon the values published in the above mentioned sources give $\omega = 3.85$ and 3.0×10^{-3} , the sample of viscose we used gives $\omega = 5.32 \times 10^{-3}$. These considerable variations are due to variations in chemical constitution of the fibres according to the method and conditions of manufacture. The regain of kapok is high, for a vegetable fibre; its high value of ω and its extreme lightness explain its high thermal

⁷ Urquhart and Williams, *J. Text. Inst.*, 1924, 15, T 559.

⁸ Wilson and Fuwa, *I. Ind. Eng. Chem.*, 1922, 14, 813.

⁹ *Rayon and Synthetic Yarn Handbook* (2nd Ed.), p. 356.

insulating properties since it affords adequate protection against temperature change and it is an excellent heat insulator under static conditions on account of its extreme lightness.

It is seen from Table I that the calculated times for the propagation of the temperature change are generally less than those obtained from the experimental curves. If a correction is applied to ω to allow for the fact that the regain increases with decreasing temperature at constant R.H. then the theoretical times are increased.

In conclusion it is of interest to note that the theory of the rate of propagation of temperature change is applicable not only to textiles but to any other hygroscopic material provided the surface volume ratio is large.

The authors' thanks are due to Mr. R. Bownass for assistance with the experimental work.

The authors of parts IV and V are grateful to Mr. B. H. Wilsdon, Director of Research, for his continued interest in the work, and to the Council of the Wool Industries Research Association for permission to publish these papers.

Summary.

The rates of propagation of temperature change through similar samples of different textile fibres under identical experimental conditions have been obtained. The results show that the time for the propagation of a given temperature change depends directly on the steepness of the regain-R.H. curve of the textile fibre used. Mean times, obtained from the experimental curves using the method of areas given in part IV, are compared with theoretical values.

THE PRIMARY SORPTION OF WATER BY COTTON.

BY S. M. NEALE AND W. A. STRINGFELLOW.

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Introduction and Summary.

The taking up of water vapour by cellulose has been extensively and accurately investigated by Urquhart and his collaborators, and by many others.¹ They have found that the curves of absorption against vapour pressure show marked hysteresis. They are sigmoid, being concave to the axis of pressure at low pressures, and convex at the higher pressures approaching saturation. The take-up at saturation is normally about 0.22 g./g., but is greater than this for celluloses which have undergone swelling treatments, such as mercerisation. In spite of the extensive investigation of the middle pressure range, it appears that knowledge of the earliest stages of the sorption, at pressures below one millimetre of mercury, is lacking.

The experiments now to be described, which cover sorptions up to 1.5 mg./g., are therefore put forward to provide information in this region, where it is probable that only primary sorption is involved.

It will be shown that the differential heat of sorption is constant over this range, and is 15.7 k. cal. per g. mole.

¹ See McBain, *The Sorption of Gases by Solids*, London, 1932, pp. 362-375.

Experimental Materials and Apparatus.

The cotton used consisted of 14.10 g. of 28's count two-fold Sakellaridis yarn, which had received a full technical bleach followed by a wash with dilute ammonia. Its examination showed that it had undergone the minimum of degradation :—

Copper No. (Schwalbe-Braidy)	. 0.015
Fluidity (0.5 % soln.)	. 3.8
COOH value ²	. 0.4 millicequiv/100g.
Solubility in boiling 1 % NaOH	. 0.08 % (by wet combustion of soln.).

The cotton, in uncut hank form, was contained loosely in the glass bulb R sealed to the high vacuum system shown in Fig. 1, and immersed in a thermostatically controlled water bath regulated to 0.1° C. The system was evacuated below 10^{-5} mm. by means of a rotary oil pump and a

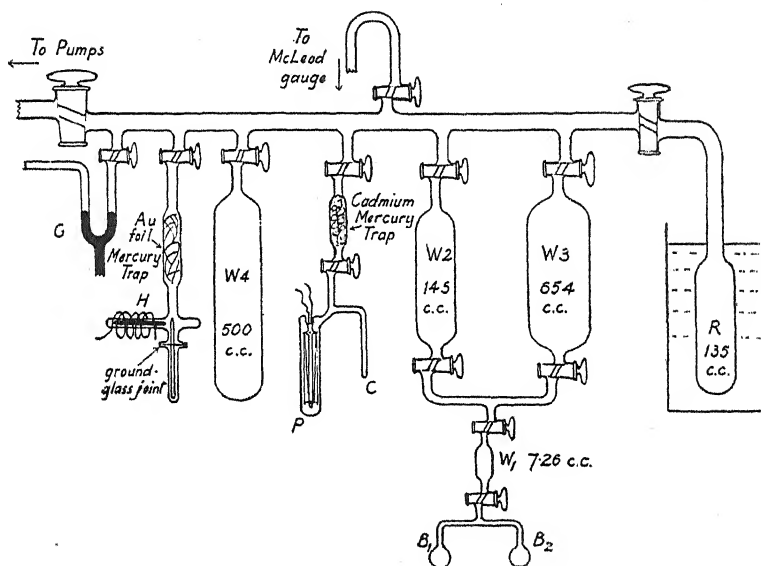


FIG. 1.

mercury diffusion pump with liquid air trap working through taps of 10 mm. bore. Measured small quantities of water were admitted to the system, either by the breaking of a sealed glass tube placed in G and containing air-free water, by means of the electro-magnetic hammer H, or more usually, by the expansion of water vapour from ice-water at 0° C. in the bulbs B into the bulbs W_1 , W_2 , W_3 , W_4 , at room temperature. Check experiments showed that these two methods supplied weights of water agreeing within 0.1 mg. The volumes of the bulbs, gauges and connecting tubes were determined either by filling with water before assembly or by successive expansions of air from volume to volume in various sequences, the pressures being read on the mercury manometer G or on the McLeod Gauge. The pressure of permanent gas in the system could be measured by the McLeod gauge, reading down to 10^{-4} mm. It was in general very small, provided that the cotton, after several hours' evacuation at 90° C., was moistened with a few milligrams of water and re-evacuated

² Neale and Stringfellow, *Trans. Faraday Soc.*, 1937, **33**, 881.

to expel air and carbon dioxide. Pressure of water vapour up to about 1 mm. Hg could be accurately read on the platinum-ribbon filament Pirani gauge P, which was kept surrounded by melting ice. This was calibrated in the manner described by Weber,³ namely by exposure to ice contained in its side bulb C, immersed in CO₂-ether mixture. The temperature of the mixture, contained in a Dewar vessel, was allowed to rise slowly from -78°C. to -15°C. , and the gauge reading taken at frequent intervals. The correction for thermal effusion pressure, described by Weber, was made. The thermometers were calibrated by means of melting ice, carbon tetra-chloride (-22.9°), mercury (-38.87°), chloroform (-63.5°), and CO₂-ether (-78.5°). The sensitivity of the gauge is indicated by the selected data given in Table 1.

TABLE 1.

Corrected pressure in P						
mm. Hg $\times 10^3$. . .	0	1.67	3.8	11.0	18.0	38.0
Pirani volts (air) . . .	2.20	2.33	2.73	3.62	4.30	5.65
" " (water) . . .	2.20	2.68	3.18	4.45	5.43	7.40
$\frac{p}{V^2 - V_0^2}$ (water) . . .	—	0.714	0.720	0.735	0.730	0.761
	76.9	168.1	476	776	—	—
	7.43	—	—	—	—	—
	9.67	13.01	17.07	19.09	—	—
	0.869	1.022	1.66	2.16	—	—

The gauge is evidently more sensitive towards water vapour than to air. This disagrees with the findings of Campbell,⁴ whose results for water were undoubtedly vitiated by failure to allow for adsorption on the glass.

Experimental Method.

The pumps were started, the temperature of the cotton was raised to 90°C. , and evacuation continued for several hours. A small amount of water vapour was then admitted to the cotton, and the pumping continued for several hours further, till the drift of the Pirani bridge galvanometer, with the pumps temporarily shut off, showed a pressure rise corresponding to an evolution of about 10^{-4} mg. of water per hour.

A measured weight of water or volume of water vapour was then admitted to the cotton, at an initial temperature which was varied from one experiment to its duplicate, and the pressure of water vapour was measured on the Pirani gauge P. Immediately after each reading of the pressure of water vapour on the Pirani gauge, the latter was shut off from the system and the gas pressure in the gauge checked by surrounding the side tube C with solid CO₂ and ether. This was found preferable to liquid air for this purpose, since traces of CO₂ were condensed by the use of liquid air, and so included in the estimated water pressure. Although the water used was distilled several times by means of CO₂-ether between the bulbs B₁ and B₂ whilst open to the pumps, and was found to be entirely free from CO₂, traces of gas presumed to be CO₂ (of the order 10^{-3} mm. to 10^{-4} mm. pressure) were invariably detected in the vapour in equilibrium with the cotton, though the amount decreased as the research proceeded.

Presumably these traces of CO₂ were not removed from the cotton during the pumping-out, but were released by preferential absorption on admission of water vapour.

After each admission of water vapour to the cotton, the pressure was read periodically till a steady value was obtained. This was reached

³ Weber, *Comm. Phys. Lab. Univ. Leiden*, 1915, No. 150.

⁴ Campbell, *Proc. Physic. Soc.*, 1920-1, 33, 289.

after overnight standing. The temperature of the cotton was then varied in steps of 10° C., and pressure readings taken. Steady readings were obtained within an hour or two after a change of temperature. The temperature range was in each case covered by variation in both directions. The system was then re-evacuated with the cotton at 90° C. before the next admission of water.

It is, of course, difficult to prove that the evacuation was effective in removing the whole of the water from the cotton. After several hours evacuation, however, the drift of the Pirani gauge bridge galvanometer with the pumps shut off indicated a rise of pressure corresponding to the evolution of only 10^{-3} to 10^{-4} mg. of water per hour. Moreover, closely agreeing duplicate pressures were obtained in repeat experiments in which after various times of evacuation the same quantity of water was admitted.

The constancy of pressure readings is illustrated by the typical data shown in Table 2, which refer to 11.43 mg. of water in the system containing the cotton at 40° C.

TABLE 2.

Temperature Sequence.	Rising.	Falling.	Rising.
Time after admission of water (days)	1	4	6
Pirani volts (V)	7.61	7.64	7.61
" " with CO_2 -ether on side tube (V_c)	2.60	2.78	2.64
$V^2 - V_c^2$	51.1	50.7	50.9
$V^2 - V_0^2 (= V^2 - V_c^2 + 2.38^2 - 2.20^2)$. . .	51.0	51.5	51.8
Pressure of H_2O , mm. Hg $\times 1000$	40.5	40.2	40.4

(Pirani volts at 10^{-5} mm. Hg = 2.20; over ice at -78° C. = 2.38).

In general the pressures observed, when a given temperature was approached from 20° C. and from 80° C. or 90° C., were, within the experimental error, identical, the figures in Table 1 being typical. Furthermore, the pressures observed were independent of the temperature at which the initial sorption of water took place.

These facts, however, do not dispose of the possibility that hysteresis could occur at these low pressures. Urquhart⁵ has shown that the amount of hysteresis depends on the extent of previous change in water content, and in no case in the present work was the desorption from saturation examined.

The most serious error resulted from the sorption of water by the glass. This was estimated by making a series of experiments in which known small amounts of water were admitted to the evacuated system in absence of cotton and the pressure-time curves determined. It is not, however, possible to make an exact allowance, since the amount of sorption by the glass varied with the length of time allowed in pumping-out, as well as with the area of glass exposed. The magnitude of the correction may be estimated from the typical figures given in Table 3. The correction for sorption on glass may be in error by as much as $\pm 20\%$, but it is only appreciable when the cotton is at a substantially higher temperature than the system as a whole.

Further correction is necessary in some cases for the thermal effusion pressure, the effect whereby the absolute pressure varies in different parts of the same system, if the temperatures of these parts are substantially different. This was estimated from the data of Weber.³ It was negligible except at the lowest pressures used, when in the most unfavourable case it amounted to 2% of the observed pressure. In the calibration of the

⁵ Urquhart, *Shirley Inst. Mem.*, 1929, 8, 27; or *J. Text. Inst.*, 1929, 20, T125.

Pirani gauge over low temperature ice, however, it amounted to 15 % in the most unfavourable case (-72°C ., $p = 1.43 \times 10^{-3}$ mm.) and fell to 1 % at -54°C . ($p = 17.8 \times 10^{-3}$ mm.). Since, however, this was the

TABLE 3.

Measured Amount of Water (mg.).		Temp. of Cotton $^{\circ}\text{C}$.	Equil. Press. mm. Hg.	Distribution of Water at Equilibrium.		
As Vapour at 4.58 mm. Hg.	Absorption on Measuring Bulbs.			Vapour.	On Glass.	On Cotton.
3.14	0.26	90	280	0.22	0.20	2.98
—	—	30	3.67	0.00	0.01	3.39
22.06	0.69	70	880	0.45	0.20	22.10
—	—	20	20.2	0.01	0.07	22.67

precise system investigated by Weber in his very careful work on the vapour pressure of ice at low temperatures, the correction, though empirical, should be reliable.

Experimental Results.

The mean equilibrium pressures, expressed in thousandths of a millimetre of mercury, are given in Table 4. On account of the fact that the amount of water present in the vapour phase, and that sorbed on the glass, varies with the temperature in each experiment (see Table 3), a small correction has been applied to make the data on each horizontal line of Table 4 correspond with the constant value for water on the

TABLE 4.

Water Absorbed, mg./g. α	Equilibrium Pressure in Thousandths of a Millimetre of Mercury.						
	20°.	30°.	40°.	50°.	60°.	70°.	80° C.
0.120	(1.08)	2.00	4.33	9.00	19.9	39.0	77.0
0.234	1.65	3.60	8.5	19.2	40.8	81	157
0.517	4.06	10.3	23.4	51	107.5	219	440
0.795	7.65	17.8	40.8	88	185	380	725
1.06	11.9	27.8	62.5	139	306	586	—
1.595	20.15	47.0	111.4	250	510	(880)	—

cotton, given in the first column. For each given sorption value the experiment was repeated at least once, and in general the repeat pressure readings agreed within 1 or 2 per cent. The variation of pressure readings, and the method of correction to a constant value of the absorption α , is illustrated by the typical data of Table 5.

In Fig. 2 $\log p$ is plotted against $1/T$. The points lie on straight lines whose slope shows that the differential heat of sorption is 15.7 k. cal. per g. mole., and is constant over the range investigated.

This value is consistent with values calculated in the same way from the measurements made at much higher pressures by Urquhart and Williams.⁶

⁶ Urquhart and Williams, *Shirley Inst. Mem.*, 1924, 3, 307; or *J. Text. Inst.*, 1924, 15, T559.

The area of the absorbing "surface" of cellulose has been variously estimated at from 1.5×10^6 cm.²/g. (for dyestuffs on cotton),⁷ to 1.36×10^5 cm.²/g. (for cobalt chloride⁸ on cotton), to 3.1×10^5 cm.²/g. (for water on wood).⁹ Assuming the area covered by a water molecule

TABLE 5. (11.43 mg. H₂O).

Temp. °C.	20.	30.	40.	50.	60.	70.	80.
Individual readings of $V^2 - V_0^2$ corr. for CO ₂ and air	10.65 10.1 9.88 10.09	25.9 22.7 24.9 24.5	51.9 50.3 51.5 51.8	102.7 98.1 101.2 102.2	172.2 170.1 176.8 —	256.3 258.0 252.3 —	333 — — 328
Mean	10.1	24.5	51.5	101.1	173	255.5	331
Mean of repeat expt.	10.0	—	52.3	101.3	175	259	340
1000p	7.75	18.0	41.0	88.0	183.5	375	710
H ₂ O on glass (mg.)	0.05	0.07	0.11	0.14	0.16	0.17	0.18
H ₂ O in vapour	0	0.02	0.05	0.09	0.18	0.24	0.35
H ₂ O on cotton	11.38	11.34	11.27	11.20	11.09	11.02	10.90
1000p corr. to 11.2 mg. ($\alpha = 0.795$ mg./g.)	7.65	17.8	40.8	88.0	185	380	725

to be 7 \AA^2 , and taking the lowest of these three estimates, it would appear that a sorption of 6 mg./g. would be needed to complete a monolayer. Any concept of a precise cellulose surface might, however, be misleading, and it would be more helpful to consider the actual number of cellulose OH groups which are accessible to reagent molecules of a particular size and shape.

TABLE 6.

	Present Data.	Urquhart and Williams.				
Sorption mg./g. :	0.12-1.6	12	19	31	43	115
— ΔU (k. cal.) :	15.7	14.0	12.9	11.8	11.5	10.4

It seems probable that the hydroxyl groups concerned will be those in the intercrystalline fringes of the fibre structure, for the X-ray evidence

⁷ Neale and Stringfellow, *J. Soc. Dyers and Col.*, 1940, 56, 17.

⁸ Howell and Jackson, *J. Chem. Soc.*, 1937, 979.

⁹ Stamm, *J. Physic. Chem.*, 1929, 33, 398.

shows that the crystallites, in which the spacing (2.6 \AA)¹⁰ of OH groups 3 and 6 of adjacent chains suggest that they are strongly linked to each other, are not penetrable by water alone. Since the spacing of the OH groups in the reactive intercrystalline fringes is not known, the steric conditions from the viewpoint of sorption cannot be laid down, but it is clear that limitations must be imposed by the immobility of the cellulose OH groups.

The value 15.7 k. cal. per mole. of water seems to be much too high for a single hydrogen or hydroxyl bond. It might be accounted for by supposing that in the stage of primary sorption each water molecule is

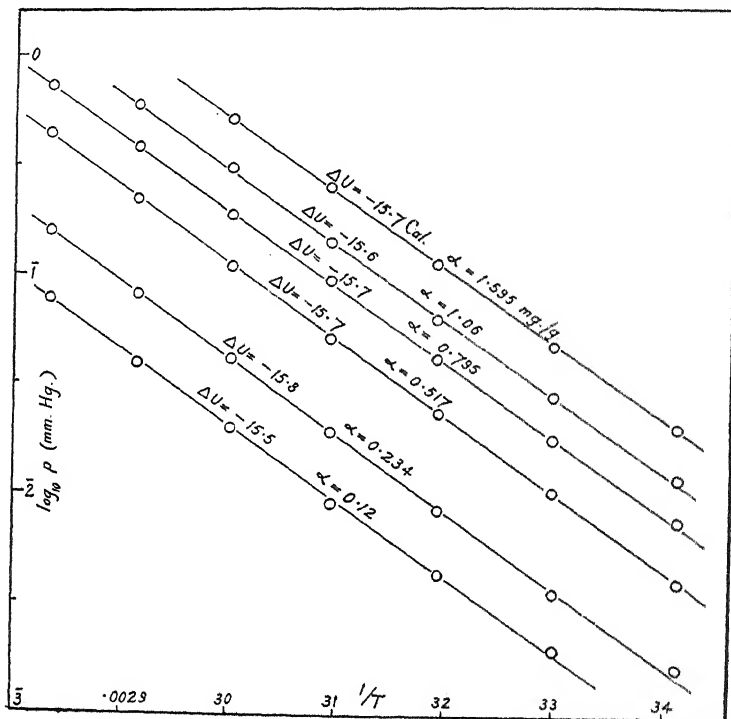


FIG. 2.

directly linked to a pair of suitably placed cellulose OH groups, for in the non-crystalline region the spacing of OH groups between one chain and another may possibly show considerable variations.

The energy per bond (7.85 k. cal.) would then be similar to that found for acetic acid, in which definite dimerisation occurs, but rather higher than the estimated values for ice and the aliphatic alcohols:—

Acetic acid ^{11, 12}	7.8 k. cal.
Ice ¹³	5.8 ± 0.2 k. cal.
Aliphatic alcohols ¹²	6 k. cal.

¹⁰ Meyer and Misch, *Ber.*, 1937, 70, 266.

¹¹ Sutherland, *Trans. Faraday Soc.*, 1940, 36, 889.

¹² Robertson, *ibid.*, 1940, 36, 913.

¹³ Fox and Martin, *ibid.*, 1940, 36, 897.

The lower bond energy in the ice structure follows from the fact that each oxygen engages two extra-distant hydrogen atoms.

As the sorption of water by cellulose increases beyond the primary stage, secondary linkages between incoming molecules and others already linked with cellulose OH groups will occur. Some of the oxygen atoms will now engage more than one extra-distant hydrogen atom, and the bond energy will fall, as reflected in the falling heat of adsorption.

Finally, towards saturation, incoming water molecules will be able to condense only on already heavily water-covered surfaces, and the thermodynamics of the process will gradually approach those of condensation in bulk. (Latent heat at 20° C. = 10.5 k. cal./mole.)

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STUDIES IN ELECTRODE POLARISATION. PART III. A NOTE ON THE THEORETICAL IMPLICATIONS OF THE RATE OF GROWTH OF POLARISATION POTENTIALS.

BY A. HICKLING.

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The observation of the way in which the potential of an electrode varies with the quantity of electricity passed during the initial building-up of overvoltage, has been widely used in recent years to throw light upon the mechanism of the polarisation process.¹ In general it has been argued that if the overvoltage is due to the accumulation of some electromotively active chemical substance at the electrode (e.g. atomic hydrogen in the case of hydrogen overvoltage), then the change of potential might be expected to be proportional to the logarithm of the quantity of electricity passed, since the amount of material liberated must be directly proportional to the quantity of electricity and, according to the Nernst equation, the potential set up should be proportional to the logarithm of the concentration of active material (or some function of it). On the other hand, if the overvoltage is due to the fact that the process of ionic discharge is slow and requires an energy of activation, then a linear variation of potential with quantity of electricity passed might be expected since, in the initial stages, the current will merely serve to charge up a double layer at the electrode surface. Thus the observation of the rate of potential build-up has seemed to afford a method of distinguishing between the two polarisation mechanisms, and since in the case of hydrogen overvoltage a linear variation of potential with quantity of electricity passed has been found, this has been held to constitute a serious objection to the atomic hydrogen theories of overvoltage.²

Although the above argument has been accepted by many workers,³

¹ See Hickling, Part II, *Trans. Faraday Soc.*, 1939, **36**, 364, for references.

² Cf. Glasstone, *Electrochemistry of Solutions*, 1937, p. 440.

³ See, for example, Baars, *Sitzungsber. Ges. Beförd. Naturwiss. Marburg*, 1928, **63**, 213; Brandes, *Z. physikal. Chem.*, 1929, **142**, 97; Erdey-Grúz and Volmer, *ibid.*, 1930, **150**, 203; Hickling, *loc. cit.*

it seems to the present author to involve a fundamental fallacy. The Nernst equation is deduced on the assumption that an electrode is in equilibrium with the ions in the solution. This can only be so if, not only do we have the electromotively active substance at the electrode, but also the necessary separation of charge, as, for example, in a double layer, which constitutes the potential difference between the electrode and the solution. Hence in considering the rate of growth of a polarisation potential, due to the accumulation of a chemical substance at the electrode, two factors must be taken into account: (a) the quantity of electricity used in setting up a concentration of active material at the electrode, and (b) the quantity of electricity used in setting up the corresponding double layer. The actual form which the $\eta - Q$ graph takes will depend upon the relative magnitudes of (a) and (b).

Thus consider the development of an overvoltage η due to the accumulation of the discharge product of a univalent ion, the ionic discharge itself being rapid and not contributing to the overvoltage in any way. Let x be the surface concentration of the product at the electrode in g. atoms per sq. cm., and x_r that at the reversible potential; also, let C be the capacity of the double layer in farads per sq. cm.

Then at any time in the initial growth of the overvoltage,

$$\frac{dx}{dQ} = \frac{1}{F} - \frac{C}{F} \cdot \frac{d\eta}{dQ},$$

and therefore

$$\frac{d\eta}{dQ} \left(\frac{C}{F} + \frac{dx}{d\eta} \right) = \frac{1}{F},$$

whence

$$\frac{1}{F} \cdot \frac{dQ}{d\eta} = \left(\frac{C}{F} + \frac{dx}{d\eta} \right) \quad \dots \quad (1)$$

Now, by the Nernst equation

$$\eta = \frac{RT}{F} \log_e \frac{x}{x_r}$$

the bulk concentration of ions in the solution being taken as constant, and therefore

$$\frac{dx}{d\eta} = x_r \cdot \frac{F}{RT} \cdot e^{\frac{F\eta}{RT}}.$$

Substituting this value in (1) gives

$$\frac{1}{F} \cdot \frac{dQ}{d\eta} = \frac{C}{F} + x_r \cdot \frac{F}{RT} e^{\frac{F\eta}{RT}}$$

and, on integration,

$$\frac{Q}{F} = \frac{C}{F} \cdot \eta + x_r \left(e^{\frac{F\eta}{RT}} - 1 \right) \quad \dots \quad (2)$$

Equation (2) gives the actual relation between Q and η during the initial build-up of overvoltage, and two special cases are apparent:

If x_r is very small, so that $x_r \left(e^{\frac{F\eta}{RT}} - 1 \right)$ is negligible compared with C/F , then

$$Q \doteq C\eta, \quad \therefore \frac{d\eta}{dQ} \doteq \frac{1}{C},$$

i.e. the potential will vary linearly with the quantity of electricity passed.

If, on the other hand, x_r is large compared with C/F , then

$$\frac{Q}{F} \approx x_r \left(e^{\frac{F\eta}{RT}} - 1 \right), \quad \therefore \frac{d\eta}{d \log_e \frac{Q}{F}} \approx \frac{RT}{F},$$

i.e. the potential will vary approximately logarithmically with the quantity of electricity passed.

Thus either a linear or a logarithmic variation of potential may occur depending upon the relative magnitudes of the quantities of electricity required to set up a certain concentration of active material at the electrode and to build up the corresponding double layer.⁴

Now consider the case of hydrogen overvoltage. From free energy considerations it can be shown that a pressure of 1 atmosphere of free atomic hydrogen would set up a potential of -1.98 v. at 25°C .⁵ i.e. at the reversible hydrogen potential the pressure of atomic hydrogen would be approximately 10^{-34} atmospheres. If, as a first approximation, we consider the atomic hydrogen to exist in the free state in a layer 10^{-8} cm. thick (approximate diameter of the hydrogen atom), this would give a value of x_r of approximately 5×10^{-47} g. atoms per sq. cm. Now C for a mercury cathode is approximately 6×10^{-6} farads per sq. cm., and therefore C/F would have a value of about 20×10^{-11} . Hence it is apparent that the value of x_r is completely negligible compared with that of C/F , and the same will be true even if there is present adsorbed hydrogen many millions of times greater in amount than the free hydrogen in equilibrium with it. Thus the potential must vary linearly with the quantity of electricity passed, as is found experimentally.

It seems likely that the same will be true of many overvoltages due to a surface accumulation of some active product; the potential will be determined by the concentration of active product, but its rate of build-up may depend upon the rate at which the corresponding double layer can be set up. Only where the quantity of electricity used in setting up the double layer is small compared with that required to bring about an appreciable change of concentration of active product at the electrode, is a non-linear dependence of potential upon quantity of electricity passed to be expected. Such cases may be comparatively few; probable examples are the potential set up by deposition of sodium in a mercury cathode, and the development of concentration polarisation.⁷

The usefulness of the observation of the rate of growth of polarisation potentials as a method for distinguishing between overvoltages due to the slow discharge of ions and to the accumulation of active products at the electrode, would thus seem to be very questionable, and it cannot be claimed that the linear variation of potential with quantity of electricity passed in the case of hydrogen overvoltage is in any way contrary to the predictions of the atomic hydrogen theory.

⁴ The nature of the double layer and the mechanism by which it is set up are quite immaterial for the development of the present point of view. It appears to involve no anomaly, however, if we simply regard the electricity passed as depositing an equivalent amount of active material at the electrode; in the initial stages a portion of this then goes into solution to form a layer of ions, the electrode being thereby left charged, and this process continues until the potential is such as to prevent further dissolution.

⁵ See Glasstone and Hickling, *Electrolytic Oxidation and Reduction*, 1935, p. 18.

⁶ Bowden and Agar, *Ann. Report*, 1938, 35, 94.

⁷ Cf. Bowden and Agar, *Proc. Roy. Soc., A*, 1938, 169, 206.

Summary.

The rate of growth of a polarisation potential due to the accumulation of an active product on the electrode surface is considered, and it is shown that a linear dependence of potential upon quantity of electricity passed is to be expected in many cases. The application of this result to the case of hydrogen overvoltage is stressed, and it is shown that the experimental results are in no way contrary to the atomic hydrogen theory.

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WOOD WATER RELATIONSHIPS, VI. THE INFLUENCE OF RAY CELLS ON THE SHRINKAGE OF WOOD.

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ABSTRACT.

In most woods the shrinkage under drying is greatest in the tangential direction, less in the radial direction and very small longitudinally. The small longitudinal shrinkage is due to the polar properties of the cellulose fibrils lying roughly parallel to the length of the tree. The asymmetry across the grain may be accounted for by the presence of ray cells which will partially inhibit the free shrinkage of the wood in the radial direction. The paper examines this explanation quantitatively and shows that in spruce the three directional shrinkages may be predicted with considerable accuracy if suitable values of the elastic constants are chosen for the fibres and ray cells and if the swelling pressure of the wood is used to determine the magnitude of the forces involved.

The shrinkage of wood is not the same in the three directions of the grain. It is greatest in the tangential (τ) direction where the shrinkage per unit change in moisture content $d\tau/dm$ lies for most woods between 0.2 and 0.4.* In the radial (ρ) direction $d\rho/dm$ is usually about half this value, while in the longitudinal (λ) direction $d\lambda/dm$ is much smaller, amounting to about 1/50th of the tangential. It is difficult to measure $d\lambda/dm$ accurately, and in standard tests it is not usually attempted. These differences in shrinkage may be accounted for by the presence of ray cells in the wood, and the purpose of the paper is to examine this hypothesis quantitatively.

The following paragraphs explain the structure of wood in so far as it affects the present discussion. This is an over-simplified picture, and the reader is referred to a Forest Products Research Record,¹ *The Growth and Structure of Wood*, for a brief but accurate account of the botanical structure.

* Shrinkages are expressed as the change in length per unit length of the green (*i.e.* water-saturated) dimensions and moisture contents as weight of water present per unit dry weight of the wood. Both ratios are frequently expressed as percentages.

¹ B. J. Rendle, *The Growth and Structure of Wood*, Forest Products Research Records No. 21 (1937), H.M. Stationery Office, 6d. net.

Wood is composed of hollow cells, of which the majority lie parallel to the length of the tree and give the wood its characteristic strength along the grain. These cells are not all of one size or type, but for the sake of simplicity it is proposed here to call all the longitudinal cells "fibres" and to assume that average properties may be assigned to a single typical fibre. A minority of cells lie horizontally and radially, penetrating between the fibres without cutting through them. These are called ray cells, and if examined on a tangential section of wood, where they appear in cross-section, they are seen to be in groups of a few cells wide and several in height, forming tall, flat plates as in Fig. 1, or lenticular bundles. In a transverse section they can be seen extending from the centre to the outside of the tree. No cells lie parallel to the tangential direction in the tree.

The construction of a single fibre should also be briefly explained. The cell has a thin, primary wall or outside casing and a much thicker secondary wall inside. Ritter² has shown by chemical dissection that, in the fibres, the crystallite portion of the walls consists of fine fibrils, those in the secondary walls lying roughly parallel to the axis of the cell, and hence to the length of the tree also, while in the primary wall they are bound round the others in a flat spiral, like the binding on a cricket-bat handle, thus preventing dispersion of the secondary fibrils under excessive swelling. As with the tree, so with the fibre and with the fibril itself, the greatest strength is longitudinal and practically all the swelling occurs transversely.

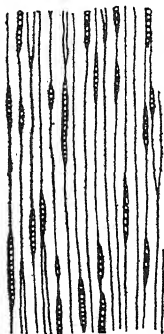


FIG. 1.

In a single fibre there is no obvious asymmetry in the transverse section, and from the nature of its construction it appears unlikely that any asymmetry would occur except for variations in the thickness of the cell wall; thus the properties of the single fibre alone cannot account for the asymmetrical shrinkage of wood. If, however, we ascribe to the ray cells, elastic properties similar to those of the fibres (in having high axial and low transverse strength), the differences between the λ , ρ and τ shrinkages are easily accounted for qualitatively in that the small proportion of strong rays inhibit the radial shrinkage without appreciably increasing the longitudinal. This may be termed the "classical" explanation of asymmetrical shrinkage and has been generally accepted.

Recently, however, this explanation has been subjected to criticism, notably in a later paper by Ritter.³ He studied single cells under crossed nicols with a selenite compensator, which shows a yellow coloration when the crystallite fibrils are parallel to a marked direction on the compensator, and blue when they are perpendicular to this direction. He publishes very striking coloured photomicrographs which show that in the fibres the crystallites lie parallel to the long axis, while in the rays they appear to be at right angles to the axis. In other words, in a radial section showing rays and fibres as they grow in the tree, both are yellow when the compensator is orientated parallel to the length of the tree which is at right angles to the rays. This arrangement

² G. J. Ritter, *Paper Trades Journal*, 1935, 101, 264.

³ *Ibid.*, 1939, 108, 33.

should give the rays a large axial and small transverse shrinkage and should undermine the classical explanation of shrinkage.

In support of this observation Ritter measures the shrinkage of dissected ray cells and finds that they shrink three or four per cent. along the axis and very little in height. This is experimentally in direct contradiction to other measurements by Clarke,⁴ who found that the axial shrinkage of ray cells was small compared to the shrinkage in height (being usually about a third), except in oak, where they were nearly equal. These contradictory results may be due to differences in species, but in any case it is evident that Ritter's shrinkage measurements cannot be accepted out of hand. His conclusions from the polarised light experiments, however, call for comment, because a preponderance of *thickness* determines the colour in the microscope, whereas a preponderance of *strength* determines the swelling. The spirally-wound fibrils in the primary wall of the fibre do not show up in the compensator, since they make a very thin layer, although in fact they exert considerable restraint on the lateral expansion of the secondary fibrils, so there may well be a small proportion of axial fibrils in the rays also, sufficient to restrain the axial expansion of the spiral fibrils, without themselves being visible in the microscope. The longitudinal Young's modulus of wood is some 25 times greater than the tangential value, and we may expect an even greater disparity between the elasticities of the fibrils parallel and perpendicular to their length, so that a very small proportion of longitudinal elements would greatly reduce the axial shrinkage of the rays.

This suggestion is to some extent borne out by Ritter's plate showing the colours when the compensator is at right angles to the fibres and parallel to the rays, where on this theory the colour should be pure blue. There are in fact distinct tinges of yellow on both fibres and rays, suggesting the presence of fibrils parallel to the compensator at this orientation. The greater sensitivity of the eye to yellow light than to blue may well account for the apparent absence of blue colour in the other position.

Other explanations of asymmetric shrinkage have been given, such as that of Frey Wyssling,⁵ who suggests that it is due to the varying density of the wood between spring and summer wood, and it is not my intention to discredit alternative explanations of anisotropic shrinkage, as it is clearly necessary to devise more conclusive experiments on ray shrinkage. If, however, the "classical" theory is to merit serious criticism, it should be put on a quantitative footing. This is the purpose of the present paper.

The hypothesis underlying the author's work on wood-water relationships is that the change in external form of wood, following a change in humidity, is brought about solely by the action of the swelling pressure which acts hydrostatically on the whole structure, and it has already been shown⁶ that it is possible to predict the volume compressibility of wood from the volume shrinkage, at any rate approximately. Thus, since the swelling pressure is uniform, the differences between the shrinkages in the three directions of the grain must be due to differences in the elastic properties of the wood. It is proposed, therefore, to use the swelling pressure to predict the three

⁴ S. H. Clarke, *Forestry*, 1930, IV, 93.

⁵ A. Frey Wyssling, *Holz als Roh und Werkstoff*, 1940, 3, 349.

⁶ W. W. Barkas, *Trans. Faraday Soc.*, 1939, 35, 388.

directional shrinkages purely from considerations of the elasticity of a standard unit cell and, since we are concerned here only with external effects, we may overlook the fact that real cells are hollow, by ascribing to a uniform prism the elastic properties necessary to produce external effects similar to those found in real wood. Owing to this simplification, the values assumed must not be taken as applicable to the wood-water aggregate, of which the hollow cells are composed.

Theory.

Calling the longitudinal axis of the cell direction 1, and any transverse axis direction 2, as in Fig. 2, we have the following elastic constants: Two Young's moduli E_1 and E_2 , and three Poisson's ratios σ_{12} , σ_{21} and σ_{22} , where, for example, σ_{12} means the ratio of the expansion along any axis 2 to the compression along axis 1, under the action of a pressure parallel to 1. For brevity we shall denote these Poisson's ratios as σ_1 , σ_2 and σ_3 respectively.

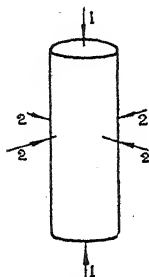


FIG. 2.

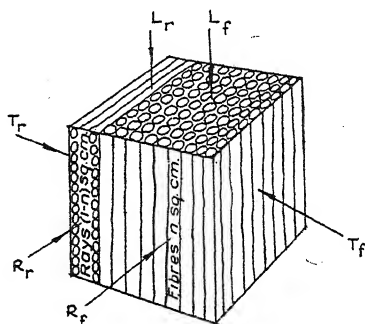


FIG. 3.

With this unit we can build an idealised wood, as in Fig. 3,* in which the majority of cells lie parallel to the longitudinal (λ) axis of the tree, while some are grouped as rays with the 1 axis parallel to the radial (ρ) direction and lying between the groups of longitudinal cells.

For the purposes of mathematical treatment imagine that the rays and fibres are not stuck together as in real wood, but are free to shrink independently. In the longitudinal and radial directions of real wood the strain or nett shrinkage of the fibres is the same as that of the rays, so in the model we must postulate separate pressures L_f , L_r ; R_f , R_r ; T_f , T_r acting parallel to the λ , ρ and τ directions in the tree, on the fibres (f) and rays (r) respectively, in order to produce this equality of shrinkage. Let there be n c.c. of fibres, and $(1 - n)$ c.c. of rays, per c.c. of wood. Thus n is also the proportion of fibres appearing on the tangential and longitudinal faces of a unit cube of wood. Let ΔL , ΔR and ΔT be the average pressures acting on the cube as a whole and parallel to the three principal axes, then from Fig. 3 it can be seen that under the action of these pressures

$$\left. \begin{aligned} n\Delta L_f + (1-n)\Delta L_r &= \Delta L \\ n\Delta R_f + (1-n)\Delta R_r &= \Delta R \\ \Delta T_f &= \Delta T_r = \Delta T \end{aligned} \right\} \quad (1)$$

* Compare with Fig. 6 of reference 1.

Under the action of these postulated pressures the nett contractions $\Delta\lambda_f$, $\Delta\rho_f$ and $\Delta\tau_f$ of the group of fibres, and $\Delta\lambda_r$, $\Delta\rho_r$ and $\Delta\tau_r$ of the group of rays are given by separate general equations as follows :—

<i>Fibres.</i>				<i>Rays</i>			
<i>Direction of stress</i>	λ	ρ	τ	<i>Direction of stress</i>	λ	ρ	τ
Displacement				Displacement			
$\Delta\lambda_f =$	$\frac{1}{E_1}\Delta L_f - \frac{\sigma_2}{E_2}\Delta R_f - \frac{\sigma_3}{E_2}\Delta T_f$			$\Delta\lambda_r =$	$\frac{1}{E_2}\Delta L_r - \frac{\sigma_1}{E_1}\Delta R_r - \frac{\sigma_3}{E_2}\Delta T_r$		
$\Delta\rho_f =$	$-\frac{\sigma_1}{E_1}\Delta L_f + \frac{1}{E_2}\Delta R_f - \frac{\sigma_3}{E_2}\Delta T_f$			$\Delta\rho_r =$	$-\frac{\sigma_2}{E_2}\Delta L_r + \frac{1}{E_1}\Delta R_r - \frac{\sigma_3}{E_2}\Delta T_r$		
$\Delta\tau_f = n\left\{-\frac{\sigma_1}{E_1}\Delta L_f - \frac{\sigma_2}{E_2}\Delta R_f + \frac{1}{E_2}\Delta T_f\right\}$				$\Delta\tau_r = (1-n)\left\{-\frac{\sigma_2}{E_2}\Delta L_r - \frac{\sigma_1}{E_1}\Delta R_r + \frac{1}{E_2}\Delta T_r\right\}$			

and the directional strains λ , ρ and τ in the wood as a whole are given by :—

$$\left. \begin{aligned} \Delta\lambda &= \Delta\lambda_f = \Delta\lambda_r \\ \Delta\rho &= \Delta\rho_f = \Delta\rho_r \\ \Delta\tau &= \Delta\tau_f + \Delta\tau_r \end{aligned} \right\} \quad . \quad . \quad . \quad (3)$$

In the particular case of $L = R = T = p$ then λ , ρ and τ should, on the initial hypothesis, be identical with the directional shrinkages of the wood under the action of the swelling pressure p .

If we use equation (1) to substitute L_f for L_r and R_f for R_r in (2), and if from equation (3) we put $\lambda_f = \lambda_r$ and $\rho_f = \rho_r$, we obtain two equations for L_f and R_f , namely :—

$$\left. \begin{aligned} \Delta L_f \left\{ (1-n) \frac{1}{E_1} + n \frac{1}{E_2} \right\} - \Delta R_f \left\{ (1-n) \frac{\sigma_2}{E_2} + n \frac{\sigma_1}{E_1} \right\} \\ + \left\{ -\frac{1}{E_2}\Delta L + \frac{\sigma_1}{E_1}\Delta R + (1-n) \left(\frac{\sigma_3}{E_2} - \frac{\sigma_2}{E_2} \right) \Delta T \right\} = 0 \\ - \Delta L_f \left\{ (1-n) \frac{\sigma_1}{E_1} + n \frac{\sigma_2}{E_2} \right\} + \Delta R_f \left\{ (1-n) \frac{1}{E_2} + n \frac{1}{E_1} \right\} \\ + \left\{ \frac{\sigma_2}{E_2}\Delta L - \frac{1}{E_1}\Delta R - (1-n) \left(\frac{\sigma_3}{E_2} - \frac{\sigma_2}{E_2} \right) \Delta T \right\} = 0 \end{aligned} \right\} \quad . \quad (5)$$

Writing these as

$$\left. \begin{aligned} a_1\Delta L_f + b_1\Delta R_f + c_1 &= 0 \\ a_2\Delta L_f + b_2\Delta R_f + c_2 &= 0 \end{aligned} \right\} \quad . \quad . \quad (6)$$

the solutions are :—

$$\Delta L_f = \frac{c_2b_1 - c_1b_2}{a_1b_2 - a_2b_1} \quad \text{and} \quad \Delta R_f = \frac{a_2c_1 - a_1c_2}{a_1b_2 - a_2b_1} \quad . \quad (7)$$

By usual elastic theory $\frac{\sigma_1}{E_1} = \frac{\sigma_2}{E_2}$ so that the constants a_2 and b_1 each reduce to $-\frac{\sigma_1}{E_1}$.

These equations give both the elastic and shrinkage properties of the wood.

Elastic Properties.—Of the constants in equations (5) and (6), only c_1 and c_2 are affected by the forces applied. If only L is acting ($\Delta R = \Delta T = 0$ and $\Delta T_f = \Delta T_r = 0$), then $c_1 = -\frac{1}{E_2}\Delta L$ and $c_2 = \frac{\sigma_2}{E_2}\Delta L$.

After using these values to solve for $\frac{dL_f}{dL}$ and $\frac{dR_f}{dL}$ in (7), equation (1) is written as

$$\left. \begin{aligned} \frac{d\lambda}{dL} &= \frac{1}{E_1} \frac{dL_f}{dL} - \frac{\sigma_2}{E_2} \frac{dR_f}{dL} \\ \frac{d\rho}{dL} &= -\frac{\sigma_1}{E_1} \frac{dL_f}{dL} + \frac{1}{E_2} \frac{dR_f}{dL} \\ \frac{d\tau}{dL} &= n \left\{ \frac{dL_f}{dL} - \frac{dR_f}{dL} \right\} \left\{ \frac{\sigma_3 - \sigma_2}{E_2} \right\} - \frac{\sigma_3}{E_2} \end{aligned} \right\} \quad (8L)$$

If only R is acting ($\Delta T = \Delta L = 0$ and $\Delta T_f = \Delta T_r = 0$), then $c_1 = \frac{\sigma_1}{E_1}\Delta R$ and $c_2 = -\frac{1}{E_1}\Delta R$, giving $\frac{dL_f}{dR}$ and $\frac{dR_f}{dR}$. Substitutions in (1) then give

$$\frac{d\lambda}{dR}, \quad \frac{d\rho}{dR} \quad \text{and} \quad \frac{d\tau}{dR} \quad (8R)$$

If only T is acting ($\Delta L = \Delta R = 0$ and $\Delta T_f = \Delta T_r = T$), then $c_1 = -c_2 = (1-n) \left\{ \frac{\sigma_3 - \sigma_2}{E_2} \right\} \Delta T$, giving $\frac{dL_f}{dT}$ and $\frac{dR_f}{dT}$. Substitutions in (1) then give

$$\frac{d\lambda}{dT}, \quad \frac{d\rho}{dT} \quad \text{and} \quad \frac{d\tau}{dT} \quad (8T)$$

Finally, if all pressures are equal ($\Delta L = \Delta R = \Delta T = \Delta p$), then

$$\begin{aligned} c_1 &= \left\{ -\frac{1}{E_2} + \frac{\sigma_1}{E_1} + (1-n) \frac{\sigma_3 - \sigma_2}{E_2} \right\} \Delta p \\ c_2 &= \left\{ \frac{\sigma_2}{E_2} - \frac{1}{E_1} - (1-n) \frac{\sigma_3 - \sigma_2}{E_2} \right\} \Delta p \end{aligned}$$

giving $\frac{dL_f}{dp}$ and $\frac{dR_f}{dp}$.

Substitutions in (1) then give

$$\frac{d\lambda}{dp}, \quad \frac{d\rho}{dp} \quad \text{and} \quad \frac{d\tau}{dp} \quad (8p)$$

The elastic constants of the wood are derived from the above equations (8) as follows:—

$$E_L = \frac{dL}{d\lambda}; \quad \sigma_{LR} = -\frac{d\rho}{dL} \frac{dL}{d\lambda}; \quad \sigma_{LT} = -\frac{d\tau}{dL} \frac{dL}{d\lambda} \quad (9L)$$

$$E_R = \frac{dR}{d\rho}; \quad \sigma_{RL} = -\frac{d\lambda}{dR} \frac{dR}{d\rho}; \quad \sigma_{RT} = -\frac{d\tau}{dR} \frac{dR}{d\rho} \quad (9R)$$

$$E_T = \frac{dT}{d\tau}; \quad \sigma_{TL} = -\frac{d\lambda}{dT} \frac{dT}{d\tau}; \quad \sigma_{TR} = -\frac{d\rho}{dT} \frac{dT}{d\tau} \quad (9T)$$

and the hydrostatic compressibility

$$\beta = \frac{d\lambda}{dp} + \frac{d\tau}{dp} + \frac{dV}{dp} \quad (9p)$$

Shrinkage Properties.—If the author's hypothesis is correct then $\frac{d\lambda}{dp}$, $\frac{d\tau}{dp}$ and $\frac{dV}{dp}$ will also be the directional shrinkages of the wood per unit change of swelling pressure p .

By Porter's equation,⁷ $\frac{dp}{dh} = \frac{v}{s} = \frac{RT}{Ms}$, where s is $\frac{dV}{dm}$, the change in volume for unit change of moisture content of the gel of which wood is composed (*i.e.* the wood-water aggregate). For present purposes where only 60 % relative humidity ($h/h_0 = 0.6$) is considered,* it will be sufficiently accurate to put s equal to unity. The slope of the usual (moisture content; vapour pressure) isothermal gives $\frac{dm}{d(h/h_0)}$; thus the directional shrinkages per unit change in moisture content are given by

$$\frac{d\lambda}{dm} = \frac{d\lambda}{dp} \frac{dp}{d(h/h_0)} \frac{(dh/h_0)}{dm} \quad (10)$$

and similarly for dp/dm , $d\tau/dm$ and for the volume shrinkage dV/dm , where $\frac{d\lambda}{dp}$ etc. are given by (8p) above.

Tests of Equations.

It remains therefore to choose suitable values for the elastic constants of the unit cell. Taking Sitka spruce wood as illustration, because the proportion of rays is small, we can *provisionally* assume that $n = 1$, whence

$$E_1 = E_L, E_2 = E_T \text{ and } \sigma_1 = \frac{\sigma_{LR} + \sigma_{LT}}{2}.$$

In addition we have $\sigma_2 = \frac{E_2}{E_1} \sigma_1$.

As regards σ_3 , this is the lateral expansion for a perpendicular lateral compression of a hollow tube. Price⁸ has shown that for a tube with the wall thin enough to be subjected to "inextensional" distortion, the ratio should be approximately 0.92. As the wall thickness increases, σ_3 will obviously approach the Poisson's ratio of the solid material of which the tube is made, and this is likely to be considerably less than 0.92.

In the case of Sitka spruce, the cell-space ratio (*i.e.* the proportion of voids to the total volume) is about 75 % at normal humidities, which shows that the average thickness of the cell wall is about 13.5 % of the radius of the cell and may be considered thin. The value of σ_{RT} for spruce wood has been measured by Golder⁹ in this Laboratory,

* The slope of the (moisture content; shrinkage) curve is almost constant below 80 % humidity so that 60 % serves as a representative value for a considerable range of moisture contents.

⁷ A. W. Porter, *Proc. Roy. Soc., A*, 1907, 79, 519.

⁸ A. T. Price, *Phil. Trans. Roy. Soc., A*, 1928, 228, 1.

⁹ H. Q. Golder and W. W. Barkas, *Nature*, 1938, 141, 874.

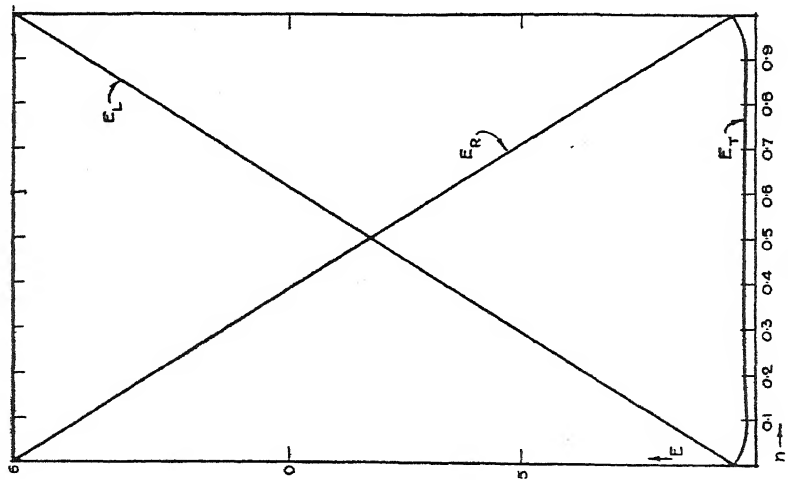


FIG. 4.

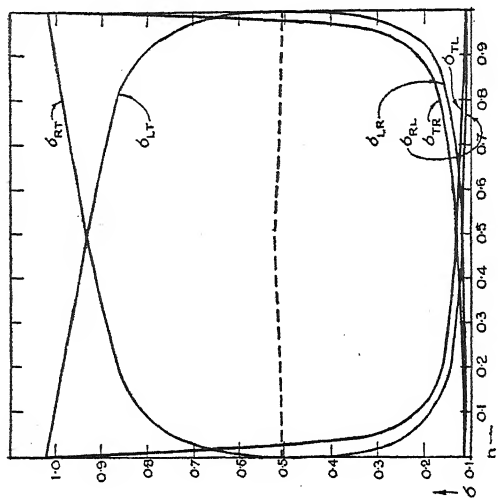


FIG. 5.

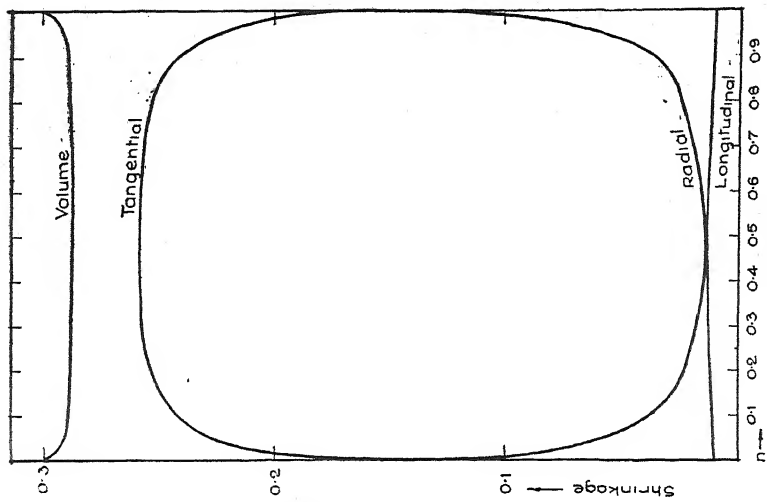


FIG. 6.

The most striking features of these curves are (1) the rapid changes in $d\tau/dm$ and $d\rho/dm$ when n has extreme values near 0 or 1, so that the ratio of these, $d\tau/d\rho$, will be very sensitive to the choice of n ; and (2) despite this, the volume shrinkage dV/dm is very nearly independent of n .

Equations (11) and (12) make it possible to correct the provisional values chosen for the unit cell. These more exact values for spruce are:—

$$\begin{array}{lll} E_1 = 1.65 \times 10^5 \text{ bars} & E_2 = 0.04 \times 10^5 \text{ bars} & n = 0.982 \\ \sigma_1 = 0.41 & \sigma_2 = 0.00984 & \sigma_3 = 0.92 \end{array}$$

From these, the calculated values of n and of the shrinkages are given below and compared with the average standard shrinkages obtained here experimentally on consignment 36 of spruce.

TABLE I.

	n .	$d\lambda/dm$.	$d\rho/dm$.	$d\tau/dm$.	dV/dm .	$d\tau/d\rho$.
Calculated . .	0.982	0.0095	0.085	0.198	0.293	2.33
Experimental .	0.927 ¹¹	—	0.125	0.250	0.375	2.00

It appears therefore that the "classical" theory of asymmetrical shrinkage is quantitatively acceptable in the case of Sitka spruce.

Wood being a variable material, it is very probable that other equally reliable elastic data might not give such good agreement, but even approximate agreement could hardly be accidental when it is remembered that the shrinkages have been calculated from purely elastic data in which the pressures were derived from the thermodynamic relationships of gels, and without reference to any shrinkage measurements. As will be shown later, the calculated shrinkages can be increased by a slight decrease in σ_3 . The value of n , which was calculated solely from the three Young's moduli of wood, does not coincide with the observed value, but, in view of the agreement in the ratio of tangential to radial shrinkage $d\tau/d\rho$ (which appears from Fig. 2 to be a sensitive test of n), it would seem that the calculated value of n is "elastically" more nearly correct than the observed value, which would make $d\tau/d\rho = 5.2$. This discrepancy between the values of n can be reconciled by assuming that the ray cells are either thinner walled or are made of inherently weaker material than the fibres. The latter explanation would fit in with Ritter's³ observations on the fibrillar arrangement in the rays, provided the author's suggestion is adopted of axial fibrils being present in the rays though not visible under the compensator. If no axial fibrils are present, the rays would offer no restraining influence to radial shrinkage, and this is equivalent to making $n = 1$.

Other Woods.

(1) **Proportion of Rays.**—So far it has been assumed that $\sigma_3 = 0.92$, the value obtained by Price⁸ for the lateral compression of a thin-walled tube. With woods of greater density, and therefore of thicker cell walls,

this assumption will not be valid. In beech, for example, the ratio of average wall thickness to radius is about 0.28, or twice that found for Sitka spruce.

This limitation does not appreciably affect the method of calculating n , the proportion of fibres, by equation (12), because from equations (8) and (9) it will be seen that E_L and E_R are independent of σ_3 , so that the straight lines shown in Fig. 3 for these moduli will not be affected. The calculation of E_T involves σ_3 , but it is in any case small and has little influence on the value calculated for n .

The following table gives the 3 Young's moduli of the air-dry material for a selection of woods from Campredon's data. It also shows the proportion of rays calculated from these moduli by equation (12) and the proportion measured visually by Myer.*¹¹

TABLE II.

	E_L (bars).	E_R (bars).	E_T (bars).	Percentage of Rays ($i = n$).	
				Calculated.	Myer.
Sitka spruce . . .	162,000	7,000	4,000	1.8	7
Pine	130,000	9,500	4,900	3.3	7
Douglas fir . . .	167,000	13,200	9,200	2.4	7
Birch	167,000	11,300	6,300	3.0	13
Ash	160,000	15,400	8,200	4.5	14
Maple	102,000	15,500	8,900	6.8	16
Beech	140,000	22,900	11,600	8.1	20
Oak	54,000	21,800	9,850	21.2	28

This table shows a clear tendency for the calculated ray percentage to increase with the measured value; a closer correlation cannot be attempted seeing that n and E were not measured on the same samples. As with Sitka spruce, the value of n obtained from elastic considerations is always lower than the measured ray volume, showing that the rays are inherently weaker than the fibres.

(2) Shrinkage.

—For woods of greater density, and hence of thicker cell walls, Price's value

will not be applicable to σ_3 , so that these species cannot be used to test the shrinkage equations. As a matter of interest, the shrinkages of beech

TABLE III.

σ_3 .	$d\lambda/dm$.	$d\rho/dm$.	$d\tau/dm$.	dV/dm .
0.92	0.0055	0.017	0.045	0.067
0.80	0.0075	0.058	0.16	0.225
0.70	0.009	0.092	0.25	0.351
0.60	0.011	0.126	0.33	0.467
0.50	0.013	0.160	0.42	0.593
Exptl.	—	0.211	0.352	0.563

* It should be pointed out that Myer's observations were made on woods of American origin and that the figures given here are mostly whole-number means of all the species he gives under a particular genus. There is considerable variation in the proportion of rays between individual samples, so that only a rough comparison is possible. Other data by Huber and Prütz¹² give the ray volumes of these woods in the same order, though not with identical values.

¹¹ J. E. Meyer, *Am. Journal of Forestry*, 1922, 20.

¹² B. Huber and G. Prütz, *Holz als Roh und Werkstoff*, 1938, 1, 377.

for several arbitrary values of σ_3 were calculated from the data given above, taking $(1 - n) = 0.081$. The results appear in Table III, together with the experimental shrinkages obtained in this laboratory and averaged from several consignments of beech.

Although the ratio of tangential to radial shrinkage is not in good agreement with experimental value, the results certainly suggest that a lower value, between 0.6 and 0.5, for σ_3 would improve the shrinkage values in this case of a denser wood. A lower value would naturally be found in the case of a tube of thicker wall. It may be noted that a small reduction in σ_3 would also improve the shrinkage values for spruce in Table I.

As regards the ratio of tangential to radial shrinkage, in any system of rays and fibres, arranged as in Fig. 3, in which the axial modulus of the individual cell is much greater than the transverse, it might be assumed that $d\tau/d\rho$ would necessarily increase as the proportion of rays $(1 - n)$ increased. Experimentally, however, we find that this ratio for Sitka spruce, beech and oak (in the order of $(1 - n)$ increasing) is 2.0, 1.67 and 1.63 respectively. This point has not been fully investigated, but it has been found that the equations given do not exclude the possibility of $d\tau/d\rho$ decreasing if suitable values of the elastic constants are chosen. For example, Campredon's values for oak with 21.2 % Rays were found to give roughly equal radial and tangential shrinkages. This result is not of course in agreement with experiment, and is probably due to his E_L being very low compared with values found in this laboratory, but it is given simply to show that the derived equations are sufficiently adaptable.

Conclusions.

The purpose of this paper has been to examine quantitatively the hypothesis that the asymmetric shrinkage of wood may be due to the presence of ray cells lying at right angles to the general direction of the grain. The equations have been derived in a form requiring a knowledge of the elastic properties of an individual cell, which for simplicity have been assumed to be identical whether the cell serves as a fibre or a ray. It is not necessary to assume that both types of cell have the same dimensions. From what appear to be plausible arguments, it has been shown that the hypothesis is valid, but that in the woods examined the rays must in fact be elastically weaker than the fibres, since the observed proportional volume of rays is in every case larger than the volume calculated on the assumption of identical elastic properties in the two types.

For wood such as Sitka spruce, having thin-walled cells, where it may be assumed that σ_3 is equivalent to the "inextensional" flattening of a thin-walled cylinder, the shrinkages calculated are in agreement with those found in practice, from which it may be deduced that the hypothesis is substantially correct. For a wood such as beech with thicker walls, the calculated values of shrinkage can be brought into fair agreement with experiment, provided the value of σ_3 is decreased. This change in σ_3 is such as would occur in the case where the flattening of the cells was not "inextensional."

The methods by which n is calculated and by which the values of the E 's and σ 's are found, are admittedly empirical, but are sufficiently accurate to illustrate the use of the equations, and in this respect the

purpose of the investigation has been achieved. No attempt has been made to learn whether E_L and E_R are truly rectilinear functions of n ; whether, as appears to be the case, $\frac{\sigma_{RT}}{E_R}$ is mathematically identical with

$\frac{\sigma_{TR}}{E_T}$ for this idealised composite material; and, if so, whether these simplifications could be used to convert the equations to a form in which all the elastic constants of the cell could conveniently be derived from the known Young's moduli and shrinkages of the wood. It would not be satisfactory to attempt this if the converted equations contained terms involving the Poisson's ratios of the wood, as these are very difficult to obtain experimentally.

Finally, it may be said that the closeness of agreement between the calculated and experimental directional shrinkages of spruce, not only supports the theory that the rays are responsible for asymmetrical shrinkage, but also gives valuable additional support to the author's original hypothesis that the swelling pressure provides the forces necessary to account for the shrinkage of wood. The paper ⁶ in which this was first examined was concerned only with the changes in volume as a whole, and took no account of the directional changes. In that paper it was shown that the volume compressibility dV/dp could be predicted from the volume shrinkage dV/dm as in equation (10) above. For example, at 60 % humidity dp/dm for spruce is 0.082×10^5 so that dV/dm , from shrinkage measurements in Table I, gives a compressibility, $dV/dp = 0.375 \div 0.082 \times 10^5 = 4.57 \times 10^{-5}$ per bar. This may be compared with the compressibility measured mechanically of 4.86×10^{-5} per bar (given, in Table III of the paper referred to, as a bulk modulus of 20.8×10^4 lb. per sq. in.). This is the compressibility of the block of wood under a hydrostatic pressure acting on the wood-water aggregate; in the testing machine the pressures applied appear smaller than this, due to the area of voids in the cross-section of the block, and require correction.

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REVIEW OF BOOK.

Mercerising. By J. T. MARSH. (London: Chapman & Hall. Pp. xv and 458 with 56 plates. 32s.)

The important textile process of mercerising has been the subject of much investigation, but it is nearly forty years since a text-book on it has appeared in the English language. The copious literature references in Mr. Marsh's book show clearly how much work has been done since that time to justify his labour, if justification be needed.

Mr. Marsh was co-author of a successful work on the Chemistry of Cellulose, which was reviewed in these *Transactions* (1939, 35, 443). Let us at once say that, of the trifling blemishes then mentioned, no serious

comment need be made this time, although occasionally Mr. Marsh's mind runs more rapidly than his pen—or his dictaphone—as witness this sentence at the foot of page 23: "About fifty civil prosecutions were pending on the decision, including the firm of Kleinewefers Söhne. . . ." However, there is never doubt as to the author's meaning, and such matters will be cleared up in further editions.

The book starts with a 27-page historical introduction; with fitting dramatic sense the opening words are those of the British Letters Patent Card specification (No. 13,296 of 1850) of Mercer which are given *in extenso*; forty years later Lowe discovered the effect of "mercerising" cotton under tension which gives to the fibre that lustre (and those other valuable properties) which the man in the street associates with "mercerised" fabric; Lowe's patent specification No. 4452 of 1890 is also given in full. This part of the book is full of interest. Mercer's fundamental invention came at a time when one main raw material (caustic soda) was still expensive and for various other reasons the textile industry was not ripe for it, and consequently his reward was meagre. Forty years later, Lowe made what, at first thought, seems to be a trifling improvement upon Marshall's invention and, the nineties proving receptive, reaped a proper reward.

Part II of the book (64 pages) is devoted to general description of the effects of mercerising on cotton. Copious references are given to the many papers in scientific journals which are so well summarised. Part III (The Mercerising Process) falls naturally into place. It develops the theoretical and practical considerations which appear in Part II, describes the types of machinery used, and extends the application of the process to yarn and cloth, and to other fibres than cotton.

The later Parts: IV (Native Cellulose and Hydrate Cellulose), V (Theoretical Aspect of the Action of Alkali), VI (Adsorptive Capacity), and VII (the Efficiency of the Process), will be of particular interest to readers of these *Transactions*. They summarise much recent work which has been scattered over the literature, much of it in the *Journal of the Textile Institute*, some in these *Transactions*, some in the *Journal of the Society of Chemical Industry*, the *Journal of the Society of Dyers and Colourists* and, of course, in Continental and American publications. Mr. Marsh is to be congratulated on the width of his research and on the readable manner in which he has performed the long-overdue task of collating this mass of information. The volume is not all of the "scissors and paste" variety, however. The author has views, and he expresses them, and when he records the work and opinions of others he gives chapter and verse.

Needless to say, coming from the house of Longmans, the volume is excellently produced and well and clearly printed; particular praise should be given to the reproduction of the 265 figures with which it is illustrated.

2. FEB. 1942

THE INFLUENCE OF GELATIN ON THE PRECIPITATION OF SILVER CHROMATE. PART IV. THE COMBINATION OF GELATIN WITH SILVER IONS.

BY T. R. BOLAM AND K. F. MACBEAN.

Received 11th July, 1941.

Potentiometric measurements with the silver electrode show that the addition of gelatin to an aqueous solution of silver nitrate reduces the activity of the silver ions.^{1, 2, 3, 4, 5, 6, 7, 8} This effect could arise from chemical combination of the silver ions with the protein, or from the operation of interionic forces. That combination does occur is indicated by the observation of Northrop and Kunitz⁹ that when equilibrium is reached between a solution of isoelectric gelatin and a solution of silver nitrate, separated by a membrane permeable only to the silver salt, the concentration of silver is higher on the gelatin side of the membrane, and the sign of the membrane potential shows that the protein has become positively charged. Bolam and Mackenzie³ found that the conductivity of a gelatin solution containing silver nitrate is less than that of a comparable solution containing potassium nitrate, a result which further supports the view that combination takes place.*

From the quantitative point of view, none of the above methods is entirely satisfactory, since each gives only the sum of the effects produced by combination and other factors. Thus estimation of the amount of combination depends upon the particular assumption made in regard to the extent of interionic action, and is correspondingly uncertain. In the present paper an account is given of results obtained by a method which measures directly the amount of combination. As will be shown, the method was developed in the course of a study of the influence of gelatin upon the precipitation of silver chromate. The effects of pH , deamination, hydrolysis and other factors upon both the combining capacity and the inhibitive action of the protein were investigated.

¹ Pauli and Matula, *Biochem. Z.*, 1917, 80, 187.

² Audubert, *Comptes Rendus*, 1923, 12, 838.

³ Bolam and Mackenzie, *Trans. Faraday Soc.*, 1926, 23, 162.

⁴ Goigner and Pauli, *Biochem. Z.*, 1931, 235, 271.

⁵ Carroll and Hubbard, *U.S. Bureau of Standards Journal of Research*, 1931, 7, 811. See Schmidt, *The Chemistry of the Amino Acids and Proteins*, 1938, 695.

⁶ Kruyt and Boelman, *Koll. Beih.*, 1932, 35, 165.

⁷ Bolam and Donaldson, *Trans. Faraday Soc.*, 1933, 29, 864.

⁸ Van Hook, *J. Physical Chem.*, 1941, 45, 422.

⁹ Northrop and Kunitz, *J. Gen. Physiol.*, 1928, 11, 481.

* The well-known experiments of Loeb,¹⁰ demonstrating that the silver is not easily washed out of the gelatin on the alkaline side of the isoelectric point, do not prove conclusively the existence of combination, since the silver ions might be held electrostatically as the kations of a gelatin salt.

¹⁰ Loeb, *Proteins and Colloidal Behaviour*, 1922, 28.

Experimental.

Gelatin.—The stock gelatin (D) was prepared in the same manner as the material employed in the previous investigations.^{3, 7, 11, 12} It yielded 16.79 % of moisture when dried at 105°, and the dried material gave 0.82 % of ash on ignition. Hydrolysis of the stock gelatin was effected by dissolving a sample in water contained in a Pyrex flask fitted with a Pyrex reflux condenser, and either heating the solution on a water-bath for one hour, or boiling it for two hours.

The following procedure was adopted for de-ashing: 200 g. of gelatin (D) was stirred with 200 ml. of 0.01 N. sodium hydroxide and washed three times by stirring with water for half-hour periods. The material was now treated for one hour with 0.01 N. acetic acid, then washed with three changes of water, again treated with 0.01 N. acetic acid, and finally washed with five changes of water. After filtering through muslin, the gelatin was perfused with absolute alcohol followed by ether, and dried by exposure to the atmosphere for 4 days. The product contained 22.02 % of moisture, and after drying at 105° gave 0.08 % of ash. In appearance it differed very little from the original gelatin.

Deamination was carried out according to the method of Hitchcock.¹³ 100 g. of de-ashed gelatin, 10 g. of sodium nitrite and 15 ml. glacial acetic acid were made up with water to give one litre of solution. This was kept, with constant stirring, at 25° for two days. The gelatin was then washed repeatedly with water, filtered off, again thoroughly washed with water, perfused with alcohol and ether, and finally kept exposed to the atmosphere for 4 days. In appearance the product was slightly darker than the original de-ashed material. It contained 16.88 % of moisture, and after drying at 105° gave 0.07 % of ash.

Particularly good distilled water was employed throughout the work.

Adjustment of pH.—The pH of the gelatin solution was varied by the addition of hydrochloric acid (ANALAR) or sodium hydroxide (ANALAR), the pH being determined colorimetrically by means of the standard buffer solutions and indicators given in Table I. In the last column of the

TABLE I.—ADJUSTMENT OF pH.

pH.	Standard Buffer Solutions.	Indicator.	Gelatin.	Volume (ml.) of Acid or Alkali Added.
				0.01 N. HCl
4.0	0.05 N. borax + 0.05 N. succinic acid ¹⁴	bromo-cresol green	deaminated	1.27
4.7	„	„	de-ashed	0.48
				0.02 N. NaOH
7.0	Sorensen's phosphate mixtures ¹⁵	phenol red	stock (D)	0.78
			hydrolysed	0.54
			de-ashed	1.18
			deaminated	2.81
9.0	0.5 N. borax + 0.1 N. potassium dihydrogen-phosphate ¹⁴	B.D.H. 8610 o-cresol	de-ashed	1.77
		phthalein	„	1.75
10.5	0.05 N. borax + 0.05 N. sodium carbonate ¹⁶	B.D.H. 9011	„	4.01
			deaminated	5.79

¹¹ Williams and Mackenzie, *J.C.S.*, 1920, 117, 844.

¹² Bolam and Mackenzie, *Trans. Faraday Soc.*, 1926, 23, 151.

¹³ Hitchcock, *J. Gen. Physiol.*, 1923-24, 6, 95.

¹⁴ Kolthoff, *J. Biol. Chem.*, 1925, 63, 135.

¹⁵ Clark, *Determination of Hydrogen Ions*, 1923, 114.

¹⁶ Kolthoff, *Säure-Basen Indicatoren*, 1932, 258.

table is shown the amount of acid or alkali required per g. of gelatin (dried at 105°) to give the corresponding pH in the first column. It was found, in agreement with previous observations, that the amount of acid or alkali so required was independent of the concentration of the gelatin solution, for the range of concentrations employed. The pH values for 1.0 % solutions of the de-ashed and deaminated gelatins were estimated to be 4.85-4.9 and 4.2 respectively.

Precipitation Experiments.—The technique was similar to that used in previous investigations of the same kind.^{11, 12, 7} For each determination two sets of solutions were prepared as follows: (1) y ml. of x N. silver nitrate + $(5 - y)$ ml. of water + 5 ml. of z % gelatin; (2) 5 ml. of 0.10 N. potassium chromate + 5 ml. of z % gelatin; x and z being kept constant, and y varied from case to case. After the solutions had been brought to the experimental temperature, by immersion in a water-thermostat at $25 \pm 0.1^\circ$, each of the first set was thoroughly mixed with one of the second. The final mixtures were kept at 25° for 2 hours, and then examined for colour. The mixture either remained yellow, or developed a reddish colour due to the formation of solid silver chromate, which was distributed, in a finely divided condition, throughout the mixture. On standing, the insoluble salt ultimately settled out.

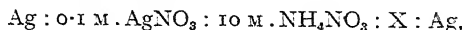
TABLE II.

Stock Gelatin. $x = 0.00667N$. $z = 1.25$ %. $pH = 7.0$.			
y (ml.).	Colour of Mixture after 2 Hours.		Nephelometer Reading. (Expt. 2.)
	Expt. 1.	Expt. 2.	
3.85	—	yellow	4.9
3.90	yellow	"	5.1
3.95	"	red	54.0
4.00	red	"	61.0
4.05	"	"	60.0
4.10	"	"	71.0
4.15	"	—	—

By the above procedure it was found possible to establish with sufficient accuracy the value of y at which silver chromate just failed to appear. This is illustrated by the typical example given in Table II.

In some instances the mixtures were examined by means of the Zeiss nephelometer, used in conjunction with the Pulfrich photometer, good agreement being obtained between the two methods of observation, as is shown by Table II. The concentration of silver corresponding to the critical value of y may be called the "threshold value" of silver nitrate for the given concentrations of gelatin ($= z/2$ %) and potassium chromate ($= 0.1/4 = 0.025 N$). In Table III are shown (under T.V.) the threshold values obtained in the present work. It is evident that $T.V. = y' \cdot x/20 N$, where y' = critical value of y . As elsewhere in the paper, concentrations of gelatin are expressed as weight (in g.) of material, dried at 105° , in 100 ml. solution, and concentrations of silver nitrate as milliequivalents per litre (m.e./l.).

E.m.f. Measurements.—The activity of the silver ion in solutions of silver nitrate containing stock (D) gelatin at pH 7.0 were determined by means of concentration cells of the type:



where X is the experimental solution. In most respects the technique was similar to that employed by Bolam and Donaldson.⁷ It was found that more reliable e.m.f. values were obtained if air-bubbles were rigidly excluded from the electrode compartments, and if the electrodes were iodised. After annealing, the electrodes were immersed in an alcoholic solution of iodine for half-an-hour, then rinsed with alcohol and dried in a stream of air. Measurements were carried out at $25 \pm 0.1^\circ$, and the

TABLE III.—SILVER NITRATE THRESHOLD VALUES.

Gelatin.	pH.	Concn. Gelatin.	T.V.	Gelatin.	pH.	Concn. Gelatin.	T.V.
Stock (D)	7.0	nil	0.127	De-ashed	7.0	0.416	0.600
		0.001	0.222			0.832	0.875
		0.00416	0.252			1.250	1.133
		0.0416	0.343			0.500	0.775
		0.100	0.415			1.000	1.175
		0.200	0.506			0.500	2.150
		0.300	0.583			0.750	3.030
		0.416	0.675			1.000	3.950
		0.832	1.002			0.500	0.630
		1.250	1.317			1.000	0.880
Hydrolysed (water-bath)	7.0	1.664	1.625	Deaminated	7.0	0.500	0.630
		0.100	0.415			1.000	0.880
						0.500	2.130
						1.000	3.900
		0.100	0.435	Stock (D)	7.0	1.000	0.675 *
		0.832	0.950			1.664	1.000 *

resistance of the experimental solution was reduced by the addition of potassium nitrate to give a concentration of 0.025 N. The data obtained are shown in Table IV, e.m.f. values being expressed in millivolts.

TABLE IV.—E.M.F. DATA.

Concn. Silver Nitrate (p).	Concn. Gelatin (C).	E.m.f.	Concn. Free Silver (q).	Silver Combined with 1 g. Gelatin (r).	C ₁₋₀₂₅ .
0.506	0.200*	139.5	0.332	0.0870	1.486
	0.832	169.2	0.106	0.0481	3.155
0.583	0.300*	138.5	0.349	0.0780	1.636
	0.832	159.5	0.154	0.0516	2.852
0.675	0.416*	138.2	0.354	0.0772	1.647
	0.832	155.2	0.182	0.0593	2.435
1.000	0.250	119.7	0.745	0.1018	0.864
	0.624	130.4	0.489	0.0819	1.387
	0.832*	135.9	0.386	0.0738	1.678
	1.024	140.6	0.322	0.0662	1.967
	1.374	153.0	0.199	0.0583	2.447
1.317	0.416	116.8	0.836	0.1155	0.683
	0.832	126.3	0.575	0.0892	1.177
	1.250*	137.7	0.360	0.0766	1.652
1.625	0.416	109.2	1.128	0.1195	0.416
	1.000	123.1	0.653	0.0972	1.000
	1.664*	137.4	0.364	0.0758	1.664

Electro-endosmosis.—The rate of electro-endosmotic flow through gelatin gels was measured in the following manner. A U-tube was filled to a fixed level with 2.0 % gelatin solution, and the gelatin allowed to gel, by immersion in iced water. The upper portions of the tube, and a horizontal capillary tube connecting them, were filled with a suitable "external solution," and a bubble of air introduced into the capillary tube. A platinum electrode was inserted in each limb close to the surface of the gel, and the apparatus was provided with soda-lime tubes to prevent the incursion of carbon dioxide. The U-tube was kept surrounded by iced water during the experiment. Determination was made of the time

* 0.515 N. potassium chromate present.

taken by the bubble to travel 3.0 cm. when a difference of potential of 100 volts was applied between the electrodes, which were 10.5 cm. apart. The mean times observed in duplicate experiments are given (in seconds) under "time of flow" in Table V. In each experiment numerous readings

TABLE V.—RATE OF ELECTRO-ENDOSMOTIC FLOW.

Gelatin (2.0 %).	pH.	Concn. Silver Nitrate.	Time of Flow.	Rate of Flow.
De-ashed . . .	7.0	—	359.0	8.80
		1.58	519.0	6.10
		—	350.0	9.00
	9.0	2.01	562.0	5.61
		—	119.0	26.50
		7.64	231.5	13.60
Deaminated . . .	7.0	—	154.0	20.50
		1.34	155.0	20.40
		—	84.0	37.60
	10.5	—	85.0	37.15
		7.44	—	—
		—	—	—

were made, the current being reversed between readings. In the last column of the table will be found values for the "rate of flow," derived from the observed time by the formula :

$$\text{Rate of flow } (\mu/\text{sec.}/\text{volt.}/\text{cm.}) = \frac{3.0 \times 10.5 \times 10^4}{\text{time of flow} \times 100}.$$

In determinations without silver nitrate, an equivalent amount of sodium nitrate was added. The total concentration of added electrolyte (including alkali) in the gel was 23.66 m.e./l. in the case of de-ashed gelatin, and 29.5 m.e./l. in the case of deaminated material. The composition of the external solution was such that the pH and the concentration of sodium nitrate were the same as in the gel, and the concentration of silver nitrate was equal to that of the free silver in the gel. Thus the external solution was not in true equilibrium with the gel, since no allowance was made for the Donnan effect. However, the results indicated that the systems were sufficiently near to equilibrium conditions for the present purpose.

A.R. or ANALAR silver nitrate, potassium chromate, potassium nitrate, and ammonium nitrate were used throughout the work.

Discussion.

The Precipitation Curve.—In the first place it is necessary to consider the precipitation data for stock gelatin at pH 7.0 (Table III). The manner in which the T.V. varies with increase in the concentration of gelatin is shown by the appropriate curve in Fig. 1. It will be seen that the curve, which may be termed the "precipitation curve," becomes linear when the concentration of gelatin reaches about 0.2 %, and that the value of the intercept on the T.V. axis of the linear portion of the curve is 0.36 m.e./l. The most reasonable explanation of this characteristic form of the precipitation curve appears to be as follows. The T.V. is greater in the presence than in the absence of gelatin, partly because the protein combines to a considerable extent with silver ions, and partly because it also promotes supersaturation with respect to silver chromate, *i.e.*, it increases the concentration of simple (free) silver ions which can remain in the presence of the given concentration of chromate ions (0.025 N.) for 2 hours without forming solid silver

chromate. With increasing gelatin concentration, both effects increase at first, but at about 0.2 % gelatin the degree of supersaturation attains its maximum value, and thereafter the free silver ion concentration remains constant at 0.36 m.e./l. At gelatin concentrations greater than 0.2 %, the amount of silver combined with unit mass of protein is given by the ratio $(T.V. - 0.36)/\text{gelatin concn.} \times 10$. Since the precipitation curve is linear in this region, the ratio is constant, which means that at a given concentration of free silver the amount of silver

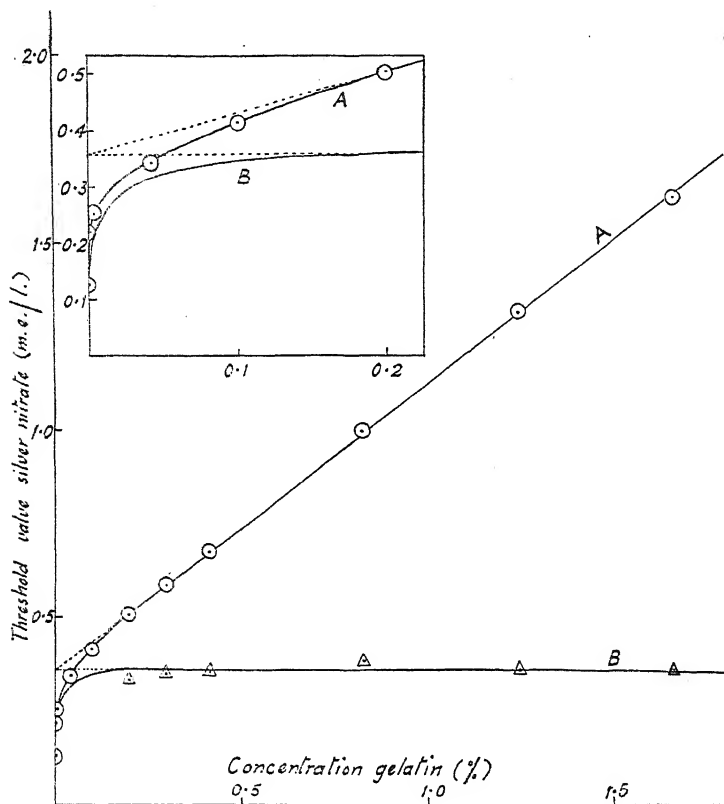


FIG. 1.—Stock gelatin at pH 7.0—A precipitation (or T.V.) curve, B free silver curve, Δ free silver from e.m.f.

combined with unit mass of gelatin is independent of the gelatin concentration.

E.M.F. Data.—The free silver ion concentrations shown in Table IV were derived from the e.m.f. values by means of the silver ion activity coefficients given by Lewis and Randall,¹⁷ the assumption being made that in the case of a gelatin solution the activity coefficient was the same as for a pure solution of silver nitrate possessing the same silver ion activity. The values marked by an asterisk (and plotted in Fig. 1) were obtained with solutions containing silver nitrate and gelatin at the same concentrations as for the linear portion of the precipitation

¹⁷ Lewis and Randall, *Thermodynamics*, 1923, 382.

curve, but containing 0.025 N. potassium nitrate instead of potassium chromate. It will be seen that all these values lie within 7% of 0.36 m.e./l., the value deduced from the precipitation data. Thus the interpretation given of the precipitation curve is confirmed.

Further confirmation is afforded by a consideration of the e.m.f. data as a whole. If p = total concentration of silver, q = concentration of free silver, r = amount of silver combined with 1 g. of gelatin, and C = concentration of gelatin, then

$$p - q = 10 \cdot r \cdot C.$$

In the fifth column of Table IV are given the values of r calculated from the experimental values of p , q and C . Now if r depends only on q , we may bring all the e.m.f. data to a common basis by supposing that $p = 1.625$ m.e./l. in every case, and calculating the values of C

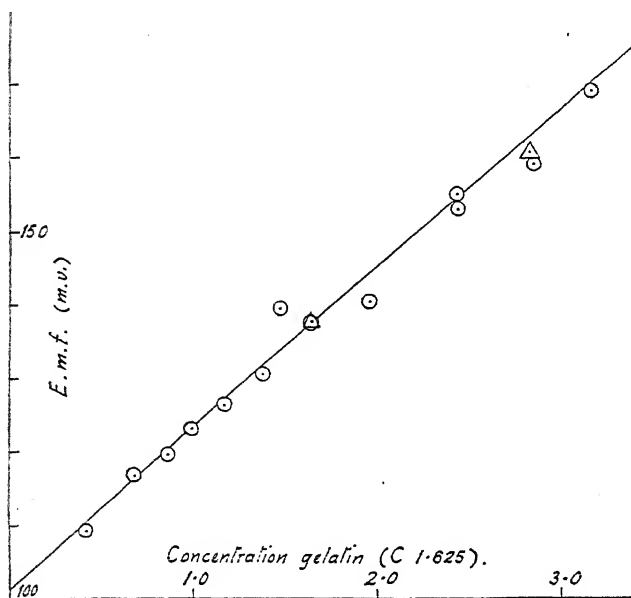


FIG. 2.
E.m.f. curve
for stock gela-
tin at pH 7.0;
○ from e.m.f.
data; △ from
precipitation
data.

which would be required to give the experimental values of q and r . For this purpose the formula becomes

$$1.625 - q = 10 \cdot r \cdot C_{1.625}.$$

The values of $C_{1.625}$ obtained are given in the last column of Table IV, and plotted against the e.m.f. in Fig. 2. It is evident that the great majority of the experimental points lie on, or close to a straight line cutting the e.m.f. axis at 101.4 mv., the calculated value for a pure aqueous solution of silver nitrate containing 1.625 m.e./l. This result fully confirms the view that, other things being equal, the amount of combination is independent of the gelatin concentration.

In two instances, with stock gelatin at pH 7.0, the threshold values were determined in the presence of 0.515 N. potassium chromate, instead of the usual much smaller concentration of 0.025 N. Also, the time of observation was increased from 2 to 3 hours. The values obtained are included in Table III. If it is assumed that they lie on the linear

portion of the precipitation curve, they are reproduced to within 2 % by the equation :

$$\text{T.V.} = 0.146 + 0.521 \times \text{gelatin concn.},$$

where 0.146 m.e./l. is the intercept on the T.V. axis, and therefore represents the concentration of free silver ion. According to this equation, when T.V. is 1.625 m.e./l., the gelatin concentration should be 1.84 %, and this should correspond to an e.m.f. of 161 mv. on the curve in Fig. 2, since this is the e.m.f. calculated for 0.146 m.e./l. free silver. Actually, 161 mv. is given by 1.75 % gelatin, which is in good

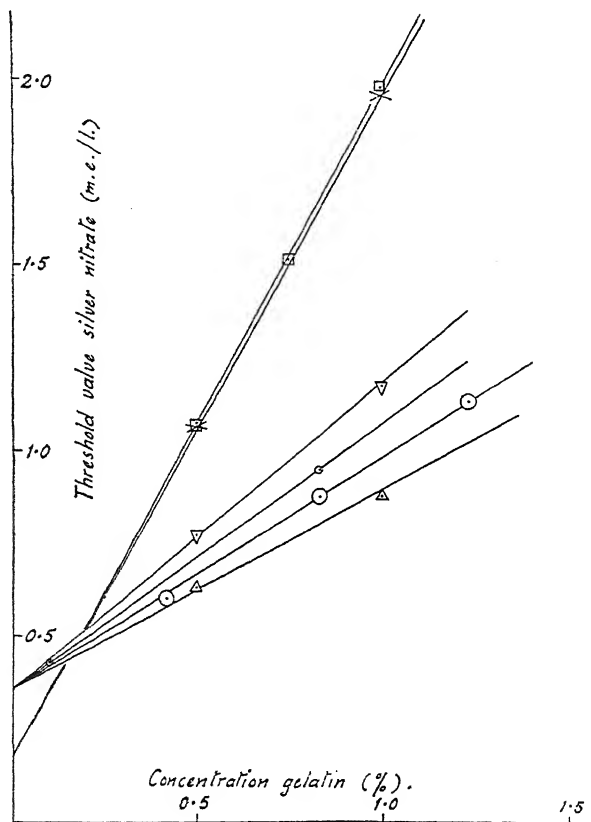


FIG. 3.—Precipitation curves ○ hydrolysed (boiled) stock gelatin at pH 7.0; ◐ deashed gelatin at pH 7.0; ▽ at pH 9.0; ◑ at pH 10.5; △ deaminated gelatin at pH 7.0; < at pH 10.5. T.V. scale to be doubled for values at pH 10.5.

agreement with the predicted value of 1.84 %, and the present interpretation of the precipitation curve therefore receives still further confirmation.

It has been indicated that the free silver ion concentrations were calculated on the assumption that the gelatin and potassium nitrate were without influence upon the activity coefficient of the free silver ion. Hence the concordance between the precipitation and e.m.f. data reveals that the reduction in the activity of the silver ion produced by the addition of gelatin is almost entirely due to actual combination of silver ions with the protein. That interionic forces should play such a minor rôle may appear surprising, but, as pointed out by Carroll

and Hubbard,⁵ the calculation of the silver ion concentration from its activity in the presence of other electrolytes is open to some question. For example, in the present work it was found that the activity of the silver ion in 0.3-0.5 N. silver nitrate was slightly increased by the addition of 0.01-0.03 N. potassium nitrate.

The Combination of Gelatin with Silver Ions.—In Fig. 3 are plotted the data given in Table III for precipitation experiments other than those with stock gelatin at pH 7.0. The figure shows that in every case the experimental points lie on a straight line cutting the T.V. axis at 0.36 m.e./l., *i.e.*, they lie on the linear portion of the precipitation curve. Hence, as previously explained, one-tenth of the slope of the line gives the amount, in milliequivalents, of silver combined with 1 g. of gelatin (m.e./g.) when the concentration of free silver is 0.36 m.e./l. The values for combined silver obtained in this way are shown in the fourth column of Table VI.

TABLE VI.—COMBINATION OF GELATIN WITH ALKALI AND SILVER.

Gelatin.	pH .	Alkali combined with 1 g. Gelatin.	Silver combined with 1 g. Gelatin.*	Charge on 1 g. Gelatin.	
				From Combination Data.	From Electroendosmosis.
Stock	7.0	—	0.076	—	—
Hydrolysed (boiled) .	7.0	—	0.071	—	—
De-ashed	4.85-4.9	0.046	—	—	—
	7.0	0.282	0.0	0.282	0.290
		0.282	0.061	0.221	0.201
	9.0	0.397	0.0	0.397	0.397†
		0.397	0.082	0.315	0.285†
	10.5	0.815	0.0	0.815	0.875
		0.815	0.358	0.457	0.449
Deaminated	4.2	0.117	—	—	—
	7.0	0.679	0.0	0.679	0.677
		0.679	0.051	0.628	0.673
	10.5	1.243	0.0	1.243	1.241
		1.243	0.354	0.889	1.226

In the case of the de-ashed and deaminated gelatins the combined silver is plotted against the pH in Fig. 4, and this figure also includes comparable data calculated from the extensive e.m.f. measurements of Carroll and Hubbard.⁵ These workers state that the silver electrode is readily poisoned in alkaline mixtures of gelatin and silver nitrate, and they place no great reliance on their measurements at pH values greater than about 8.0. In the present work also the silver electrode was found to be quite unsatisfactory at pH 9.0, the potential altering rapidly with time. Thus the precipitation method of determining the amount of combination with silver has at least one advantage over the more convenient potentiometric method, in that it can be applied to alkaline solutions.

The amounts of alkali combined with the gelatin at the different pH values have been calculated from the colorimetric data in Table I. It was assumed that the iso-electric point for the de-ashed gelatin lay

* When silver nitrate present, free silver = 0.36 m.e./l.

† Correction applied.

at pH 4.7, and that for the deaminated material at pH 4.0.^{13, 18} The values obtained are given (in m.e./g.) in the fifth column of Table VI, and they are also plotted against pH in Fig. 4. It will be seen that the form of the curve for combined silver closely resembles that for combined alkali.

The following evidence indicates that the ϵ -amino groups of the lysine residues in gelatin are free, and that the main effect of the action of nitrous acid is the removal of these groups: (a) no lysine can be

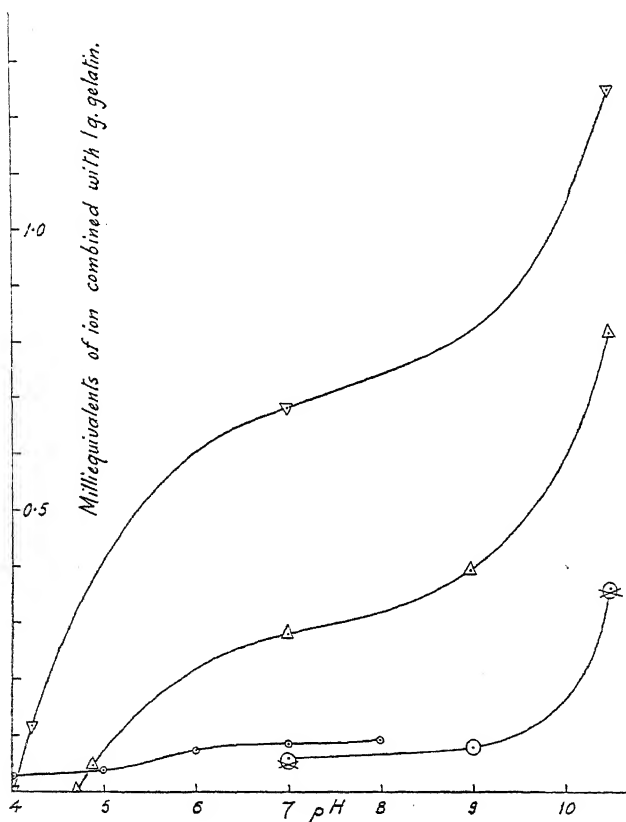


FIG. 4.—Combination with silver ions ○ de-ashed gelatin; >×< deaminated gelatin; ⊙ Carroll and Hubbard (de-ashed gelatin). Combination with hydroxyl ions; △ de-ashed gelatin; ▽ deaminated gelatin.

isolated from the acid hydrolysate of gelatin previously treated with nitrous acid;¹⁹ (b) gelatin treated with nitrous acid in the Van Slyke apparatus yields one-half of the nitrogen found in the lysine fraction of the acid hydrolysate of the untreated protein;^{13, 20} (c) on treatment with nitrous acid, the decrease in total nitrogen is equal to the nitrogen evolved in the Van Slyke apparatus;^{13, 18} (d) if benzenesulphonated gelatin is hydrolysed with formic and sulphonic acids, the amount of ϵ -amino-sulphonyl-*D*-lysine which may be isolated is equivalent to at

¹⁸ Loebel, *J. Physical Chem.*, 1928, **32**, 763.

¹⁹ Skraup and Kass, *Ann.*, 1906, **351**, 379.

²⁰ Van Slyke and Birchard, *J. Biol. Chem.*, 1913-14, **16**, 539. Dakin, *ibid.*, 1920, **44**, 499. Albaneses, *ibid.*, 1940, **134**, 467. Northrop, *J. Gen. Physiol.*, 1920-21, **3**, 715.

least 50 % of the nitrogen lost on treatment with nitrous acid; ²¹ (e) the bromine content of the compound formed by the action of *p*-bromophenyl isocyanate on gelatin usually represents 70 to 90 % of the lysine content of the protein.²²

According to Schmidt, Kirk and Appleman,²³ the value of *pK* for the dissociation of the ϵ -amino group in lysine itself is 10.53 at 25°, and Levene and Simms have obtained *pG* = 10.45.²⁴ Hence, since it appears likely that the ϵ -amino group is situated relatively far from other groups in the protein molecule, this group may be expected to dissociate in the region of *pH* 10.5.²⁵ Actually the form of the titration curve in a number of cases is consistent with this. Cohn, Green and Blanchard²⁶ obtained *pK* = 10.8 for horse carboxyhaemoglobin, Green,²⁵ *pK* = 10.5-10.7 for normal horse serum globulins, and Simms,²⁴ *pG* = 10.4-10.6 for gelatin.

Since over the *pH* range 9.0-10.5 there are large increases in the amounts of both silver and alkali bound by the gelatin, it would be reasonable, in the light of the foregoing, to suppose that the silver ions form complexes with the ϵ -amino groups (in their non-ionogenic state $-\text{NH}_2$). That in all probability cupric ions combine with gelatin in this manner is indicated by the observation of Northrop and Kunitz⁹ that the copper combining capacity of deaminated gelatin is less than that of the untreated material by an amount equivalent to the decrease in acid combining capacity, *i.e.*, to the loss in total nitrogen.^{13, 18} However, the present results show that while deamination produces a slight decrease in the silver bound at *pH* 7.0, there is no perceptible change at *pH* 10.5. Hence it would appear that either the silver ions do not combine with the free amino groups of the gelatin, or else the action of the alkali on deaminated gelatin at high *pH* values gives rise to free amino groups equivalent in amount to those removed by treatment with nitrous acid.

An alternative view is that the silver ions combine with the $\text{COO}-$ groups in the gelatin molecule, and that the increase in combination between *pH* 9.0 and 10.5 is due to the formation of such groups by hydrolysis of the protein by the alkali. According to the data quoted by Jordan Lloyd and Shore,²⁵ and by Schmidt,⁵ the carboxyl groups in unhydrolysed gelatin amount to about 0.40 m.e./g., and these groups must be fully ionised at 9.0. Hence, since the combined alkali increases by about 0.40 m.e./g. between 9.0 and 10.5, the number of $\text{COO}-$ groups will be doubled at the most, an increase which is quite inadequate to account for the fourfold increase in combined silver.

The e.m.f. curve (Fig. 4) shows that, for constant concentration of total silver,

$$\log. \text{ activity silver ion} = k_1 + k_2 \cdot \text{concentration gelatin},$$

where k_1 and k_2 are constants, k_2 being the activity of the silver ion in the absence of gelatin. It was ascertained that comparable data obtained by other workers^{3, 5, 6, 7} also conform to this relation. It was

²¹ Gurin and Clarke, *J. Biol. Chem.*, 1934, 107, 395.

²² Hopkins and Wormall, *Biochem. J.*, 1933, 27, 740, 1706; *Nature*, 1934, 134, 290.

²³ Schmidt, Kirk and Appleman, *J. Biol. Chem.*, 1930, 88, 283.

²⁴ Simms, *J. Gen. Physiol.*, 1927-28, 11, 629.

²⁵ Green, *J.A.C.S.*, 1938, 60, 1108. Jordan Lloyd and Shore, *Chemistry of the Proteins*, 1938, 303-305.

²⁶ Cohn, Green and Blanchard, *J.A.C.S.*, 1937, 59, 509.

further found that the variation of the amount of silver combined with unit mass of gelatin (as deduced from the e.m.f. curve) with change in free silver concentration, could not be expressed by Langmuir's adsorption (or combination *) equation in its simplest form. Hence it would appear that the silver is bound by more than one type of group in the gelatin molecule, and this is also suggested by the manner in which the amount of combined silver varies with the pH .

Electro-endosmosis.—In the last column of Table VI are given the values obtained by multiplying the rates of endosmotic flow (Table V) by the factor 0.033. Comparison of these values with those in the fifth column reveals that (a) in the absence of silver, the rate of flow is directly proportional to the amount of alkali combined with unit mass of gelatin; (b) in the case of de-ashed gelatin in the presence of silver nitrate, the rate of flow is directly proportional to the difference in the amounts of alkali and silver combined with unit mass of gelatin, and (c) in the case of deaminated gelatin, the addition of silver nitrate produces no effect upon the rate of flow. Thus, on the whole, the results from endosmosis are in agreement with those obtained in other ways. In the case of de-ashed gelatin at pH 9.0, the values for the charge actually found by endosmosis were less than those given in the table by 0.100. No definite reason can be given for the lack of agreement between the experimental values, but it is probably due to experimental error.

The most striking feature of the results is the difference in behaviour of the de-ashed and deaminated gelatins in the presence of silver nitrate at pH 10.5. While the charge in the case of de-ashed gelatin is decreased by an amount equivalent to the combined silver, no change is observed with the deaminated material, although the amount of combined silver is the same. In this instance the discrepancy is far greater than the probable experimental error. At present it does not seem possible to account for the phenomenon.

The Inhibitive Action of Gelatin.—It has been shown that the shape of the precipitation curve is best explained on the assumption that at constant chromate ion concentration the degree of supersaturation with respect to silver chromate does not increase indefinitely with increase in the gelatin concentration, but soon reaches a constant value. Such behaviour was indicated by the results of a previous investigation,⁷ but the data then available were not decisive since they were obtained from systems in which the concentrations of gelatin, silver nitrate, and potassium chromate were all varied together. At the same time, however, it was established that the combination of chromate ion with gelatin decreases with increase in pH (since confirmed by Van Hook⁸). This result suggested that the conditions employed in the present work would permit of variation of the gelatin and silver ion concentrations, while maintaining a constant concentration of chromate ion.

The free silver ion curve in Fig. 1 shows how the degree of supersaturation, and hence the inhibitive action of the gelatin, varies with the concentration of the protein in the case of stock gelatin at pH 7.0. It was found that the silver electrode was not satisfactory at concentrations of gelatin less than about 0.2 %, and the free silver values for the initial part of the curve were therefore deduced from the combination curve based on the e.m.f. curve in Fig. 4.

* Hitchcock (*J.A.C.S.*, 1926, 48, 2870) has pointed out that at present it is impossible to distinguish between mass law combination and adsorption which obeys Langmuir's equation.

Strictly speaking, the experiments show how the gelatin influences the degree of supersaturation which can be maintained for an "induction period" of 2 hours. It is generally accepted that the main process occurring during this period is the formation of stable crystal nuclei.^{8, 27} To be stable, a nucleus must attain a certain minimum size; otherwise it tends to disintegrate, as is shown by the high solubility of very small particles. Hence it would appear that the gelatin opposes the formation of stable nuclei, and it seems probable that the protein is adsorbed on potential nuclei and inhibits their growth by preventing the access of suitable ions. The fact that the inhibitive action of the gelatin reaches a maximum is in harmony with this view, since there will be an upper limit to the adsorption.

The inhibitive action of the gelatin would appear to resemble its protective action on sols, in the sense that a sheath is formed round incipient nuclei. Quantitatively, however, there is a marked difference. The concentrations corresponding to the "gold numbers" commonly found in the literature²⁸ vary approximately from 0.0005 to 0.0025 %, whereas the minimum concentration of stock gelatin required to give the maximum inhibitive effect at pH 7.0 is about 0.2 %.

Since in all the cases examined the intercept of the linear part of the precipitation curve has the same value, it follows that the maximum value of the degree of supersaturation is not influenced by de-ashing, deamination or hydrolysis of the gelatin, or by variation of the pH between 7.0 and 10.5. More data are required to ascertain whether the concentration of gelatin at which the supersaturation reaches its maximum value varies from case to case, although the maximum supersaturation itself remains constant. That such variation may occur is indicated by the data for boiled gelatin (Table III). The T.V. at 0.1 % gelatin appears to lie on the linear portion of the precipitation curve, which means that maximum supersaturation is attained at a much lower concentration than in the case of the unhydrolysed gelatin (= 0.2 %).

Summary.

1. The influence of gelatin on the precipitation of silver chromate may be employed to determine the combination of gelatin with silver ions.
2. The decrease in the activity of the silver ion in solutions of silver nitrate containing gelatin is almost entirely due to combination with the protein.
3. At constant free silver ion concentration, the combination of silver ions with gelatin (a) is independent of the gelatin concentration, (b) increases slowly over the pH range 7.0-9.0, but rises rapidly between 9.0 and 10.5.
4. Deamination of the gelatin slightly decreases the combination at pH 7.0, but produces no change at 10.5.
5. The results indicate that (a) if silver ions form complexes with the free amino groups of gelatin, the action of alkali on deaminated gelatin at high pH values must give rise to amino groups equivalent in amount to those removed by the action of nitrous acid (b) the increase in combined silver between pH 9.0 and 10.5 is not due to attachment of silver ions to COO—groups formed by hydrolysis of the protein.

²⁷ Jensen, *Z. physikal. Chem., A*, 1937, **180**, 93. Reitemeier and Buehrer, *J. Physical Chem.*, 1940, **44**, 552. Volmer, *Z. Elektrochem.*, 1929, **35**, 557.

²⁸ See references in Clayton, *Colloid Aspects of Food Chemistry and Technology*, 1932, 68, 69.

6. While at pH 10.5 the charge on untreated gelatin is reduced by an amount equivalent to the combined silver, no effect is observed in the case of deaminated gelatin.

7. At constant concentration of silver nitrate, the logarithm of the free silver ion concentration varies in linear fashion with change in the concentration of gelatin.

8. The inhibitive action of gelatin reaches a maximum at a low concentration of the protein.

9. The maximum inhibitive action is not affected by purification, deamination or thermo-hydrolysis of the gelatin, or by variation of the pH over the range 7.0-10.5.

10. It is probable that thermo-hydrolysis decreases the concentration of gelatin at which the maximum inhibitive action is attained.

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ON THE POLARISATION OF FLUORESCENCE OF SOME SIMPLE AROMATIC HYDROCARBONS IN SOLUTION.

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1. Directional Variations in the Absorption and the Fluorescence of Aromatic Molecules.

The crystal structures of many of the simple aromatic hydrocarbons have been analysed completely by X-ray methods by Robertson and others.¹ The molecules of these compounds are found to retain their individuality in the crystal state; their orientations in the crystals are also known. These crystals, therefore, form suitable media for studying the directional variations in the optical and other properties of the constituent *molecules*. In some recent papers Krishnan and Seshan² have studied under polarised light the absorption and the fluorescence spectra of single crystals of anthracene, phenanthrene, chrysene, dibenzanthracene, etc., whose molecules are all known to have a plane structure. From an analysis of the experimental data, Krishnan and Seshan obtain the following important results:—

(1) All the absorption bands in the visible and in the near ultra-violet regions of the spectrum are confined to that component of the electric vector, of the incident light-wave, which lies in the plane of the molecule. The component of the electric vector along the normal to the plane of the molecule is not absorbed at all.

¹ *Proc. Roy. Soc. (A)*, 1933, **140**, 79; *ibid.*, 1934, **146**, 140.

² *Current Science*, 1934, **3**, 26; *Z. Kristallog. (A)*, 1934, **89**, 538; see also Reports of the International Conference on Photoluminescence, Warsaw, *Acta Physica Polonica*, 1936, **5**, 289.

(2) Similarly, it is only the component of the electric vector of the incident light-wave that lies in the molecular plane that is capable of exciting fluorescence (provided, of course, that the wave-length is suitably short), whereas the component of the electric vector along the normal to the plane of the molecule does not excite any fluorescence.

(3) When the fluorescence is excited by polarised light whose electric vector lies in the molecular plane, the electric vector of the fluorescent radiation thus excited, also lies in the molecular plane.

2. The Nature of the Fluorescent Oscillators.

Now, all the aromatic condensed ring compounds mentioned above crystallise in the form of thin flakes. They are all monoclinic, save naphthacene which is triclinic. Hence, it is convenient experimentally in studying the absorption and the fluorescence spectra of these crystals to allow the incident light to fall normally on the crystal flake and to make observations in the forward direction. With this arrangement the electric vector of the light propagated in the crystal is along the one or the other of the two extinction directions in the plane of the crystal flake, and it is only the components along these two directions, of the electric vector of the transmitted light or of the fluorescent light, that can be studied.

Now, in all these crystals the long axes of the molecules are found to be nearly perpendicular to the plane of the crystal flake. Hence, with the experimental arrangement described above it is only those variations in the optical properties of the molecule occurring as we pass from a direction perpendicular to the molecular plane towards the short dimension in the molecular plane, which can be studied; it is not possible with this arrangement to study the variations in the molecular plane itself, to find for example whether the excitation of fluorescence will be equally efficient for all directions of the incident electric vector in the molecular plane, or again whether, in the fluorescence thus excited, the electric vector, which is known from the experiments of Krishnan and Seshan to lie in the molecular plane, corresponds to any definite direction in the plane related in a simple manner to the geometry of the molecule and to the direction of the exciting electric vector. In other words, besides the observation that the oscillators emitting the fluorescent radiations are all in the molecular plane, no information is available at present regarding the number of these oscillators, or their directions in the plane. In particular, it would be interesting to know whether these oscillators are coherent in phase among themselves, though not with the incident electric vector which excites them, or whether they radiate independently of one another.

This last question, however, can be answered easily by studying the polarisation of the fluorescence of these molecules when dissolved in highly viscous solvents. It is well known from the work of Perrin³ and others that owing to the finite duration of the molecule in the excited state, and the rotation of the molecule that will occur in this interval of time, the observed polarisation of the fluorescent light will be less than when the molecules have no rotation. Since for a given duration in the excited state the angle of rotation of the molecules will be the smaller the larger the viscosity of the solution, one may presume that the limiting value, which the observed polarisation tends to reach asymptotically

³ See *Fluorescence*, Hermann, Paris, 1931, p. 35.

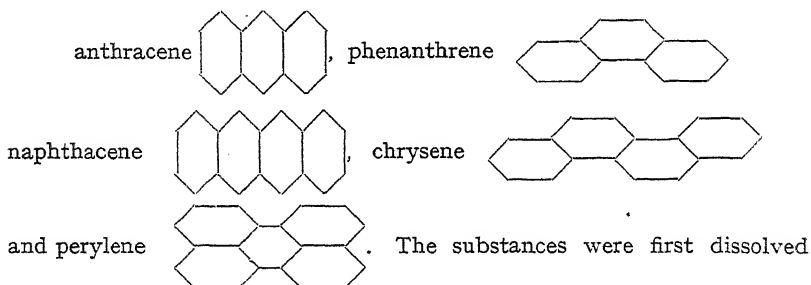
as its viscosity is increased indefinitely, will be the value characteristic of a medium in which the molecules are non-rotating, but are randomly oriented.

When the fluorescence is excited by a parallel beam of polarised light and observed along a direction perpendicular to the direction of the electric vector of the incident light, the magnitude of the above limiting polarisation for large viscosity can be easily calculated for different types of fluorescent oscillators in the molecule. In the simple case when the fluorescence is due to a single linear oscillator the polarisation can be shown to be 50 %. A set of linear oscillators radiating fluorescence independently of one another will naturally give the same polarisation as a single linear oscillator.

In the present paper are described polarisation measurements in solution, of some of the simple aromatic hydrocarbons previously studied in the crystal state by Krishnan and Seshan.

3. Experimental.

The following five plane condensed ring hydrocarbons were studied by us for their fluorescence, all of them in solution in Merck's pure glycerin of density 1.26 :—



in alcohol, and a drop of the strong alcoholic solution was added to the glycerin and mixed with it thoroughly. The glycerin solution was contained in a small cylindrical cell, fitted with plane glass windows. The cell was kept immersed in a transparent liquid bath in an unsilvered glass "thermos-flask." The incident light was polarised by passage through a nicol and focussed with the help of a long focal length lens in the centre of the cell, and the fluorescent light emitted in the forward direction was analysed for its polarisation by the well-known method of Cornu. Care was taken to ensure that the portion of the glass walls of the thermos-flask traversed by the light did not show any double-refraction as tested by the restoration of light between crossed nicols. Measurements were made at two temperatures, (1) at the temperature of the room, and (2) at the temperature of a mixture of carbon dioxide and ether evaporating at atmospheric pressure, namely -79°C .

The 3650, 4047 and 4358 groups of lines of mercury, obtained by passing the light from a mercury lamp through suitable filters, served for exciting the fluorescence. The polarisation measurements on the fluorescent light were in general made visually, using a complementary filter in the path of the fluorescent light for cutting out the incident radiations. In some of the measurements, however, the fluorescent light after passage through the double image prism (suitably oriented to separate the two principal vibrations) and nicol (so oriented as to equalise the intensities of the two images) was focussed on the slit of the spectroscope; the polarisations of

the different bands appearing in the fluorescence spectrum could thus be studied separately, by the photographic method.

We may mention immediately the following results, which make the experimental study very simple. Within the range of our experiments, (1) the polarisation is practically the same for all the fluorescent bands of a substance; (2) the polarisation of fluorescence is independent of the frequency of the incident light that excites it.

4. The Absorption Spectra of the Solutions.

Since the solubilities of these substances in glycerin are very small, it is necessary to ensure that all the substance introduced into the glycerin has gone into real solution and remains so even at the lowest temperature. In our measurements this was verified by studying the absorption spectrum of the liquid. For all these substances the absorption spectrum in the solid state is slightly shifted towards the red as compared with the spectrum of the substance in solution in glycerin, and the latter spectrum again is shifted similarly towards the red with reference to the spectrum of the substance in solution in alcohol.⁴ The positions of the absorption bands thus serve to decide uniquely whether the substance has all gone into solution in glycerin, or is partly held in suspension in glycerin in the form of fine solid particles.

Judged by this test, it was found for example in the case of chrysene, that an appreciable part of the substance introduced into glycerin by adding a drop of the strong alcoholic solution, remained undissolved, and an excess of glycerin had to be added before the whole of the chrysene could be made to go into solution.

TABLE I.

Substance in Solution.	Temp. °C.	<i>p</i> .
Anthracene . . .	30 -79	31 44
Phenanthrene . . .	30 -79	28 41
Naphthacene . . .	30 -79	34 41
Chrysene . . .	30 -79	33 42
Perylene . . .	30 -79	31 41

5. Results.

The results of the polarisation measurements on the fluorescence are collected together in Table. I. The fluorescent radiation is naturally partially polarised, with its principal directions of vibration along the direction of vibration of the incident light, and perpendicular to it, respectively. Denoting the intensities of the two components by $I_{||}$ and I_{\perp} respectively ($I_{||} > I_{\perp}$), the percentage of polarisation p is given by the usual expression

$$p = \frac{I_{||} - I_{\perp}}{I_{||} + I_{\perp}} \times 100.$$

For all the substances the value of the polarisation at the lower temperature is about 41 to 44 %, and a comparison of this with the room temperature value suggests that the limiting value of p for the infinitely viscous solution may be very close to 50 %.

⁴ P. K. Seshan, *Trans. Faraday Soc.*, 1936, **32**, 689.

We are thus led to the conclusion that in all these aromatic compounds the molecular fluorescence is due either to a single linear oscillator, or to a set of linear oscillators that radiate independently of one another.

In conclusion, the authors desire to express their grateful thanks to Professor K. S. Krishnan for suggesting the problem and for his kind interest in the work.

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ISOPIESTIC MEASUREMENTS ON SOLUTIONS OF POTASSIUM CHROMATE AND POTASSIUM DICHROMATE.

Received 19th September, 1941.

By R. H. STOKES, JEAN M. WILSON AND R. A. ROBINSON.

The activity coefficients of the alkali metal sulphates^{1, 2} increase in the order $K_2SO_4 < Na_2SO_4 < Li_2SO_4$, corresponding to values of the closest distance of approach of the ions which increase with decreasing atomic weight of the cation. It has also been shown² that the activity coefficient of $Na_2S_2O_3$ is greater than that of Na_2SO_4 but less than that of Li_2SO_4 ; the replacement of an O atom by a S atom in the anion therefore increases the size of the ion as measured by the distance of closest approach, *i.e.* the \bar{a} parameter in the Debye-Hückel equation.

TABLE I.—CONCENTRATIONS OF ISOPIESTIC SOLUTIONS OF POTASSIUM CHROMATE, POTASSIUM DICHROMATE AND POTASSIUM CHLORIDE AT 25°.

Molality.		Molality.		Molality.	
KCl.	K ₂ CrO ₄ .	KCl.	K ₂ CrO ₄ .	KCl.	K ₂ CrO ₄ .
0.09690	0.07255	1.391	1.177	3.141	2.580
0.1612	0.1242	1.413	1.198	3.147	2.585
0.2544	0.1998	1.700	1.443	3.330	2.717
0.4355	0.3500	1.725	1.464	3.339	2.725
0.4529	0.3647	1.840	1.564	3.374	2.747
0.5285	0.4282	2.128	1.798	3.481	2.826
0.5492	0.4467	2.237	1.891	3.593	2.913
0.5750	0.6233	2.319	1.957	3.774	3.032
0.8368	0.6942	2.403	2.017	4.193	3.314
1.040	0.8678	2.914	2.415	4.266	3.372
1.106	0.9265	2.993	2.472		
KCl.	K ₂ Cr ₂ O ₇ .	KCl.	K ₂ Cr ₂ O ₇ .	KCl.	K ₂ Cr ₂ O ₇ .
0.09088	0.06133	0.1933	0.1396	0.4188	0.3245
0.09150	0.06205	0.2385	0.1756	0.4754	0.3778
0.1343	0.09408	0.2741	0.2045	0.6007	0.4895
0.1456	0.1035	0.3306	0.2508	0.6238	0.5072
0.1873	0.1350	0.3534	0.2718		

¹ Åkerlof, *J. Amer. Chem. Soc.*, 1926, 48, 1160; Harned and Hecker, *ibid.*, 1933, 55, 4838.

² Robinson, Wilson and Stokes, *ibid.*, 1941, 63, 1011.

We have now made some measurements on K_2CrO_4 by the isopiestic method, in order to compare its activity coefficient with that of K_2SO_4 ; in addition we are able to report some measurements on $K_2Cr_2O_7$.

Experimental.

The salts were recrystallised from Analar material and their purity was checked by analysis. Solutions of K_2CrO_4 and $K_2Cr_2O_7$ were brought to equilibrium with solutions of KCl by the isopiestic method,³ with the results given in Table I. The solubility of $K_2Cr_2O_7$ in water at 25° was found to be 13.07 g. per 100 g. of solution or 0.5110 M, using the method of Scatchard, Hamer and Wood.⁴

Discussion.

The osmotic and activity coefficients of K_2CrO_4 were evaluated with reference to the activity coefficient of potassium chloride given previously.⁵ As the osmotic coefficients of K_2CrO_4 and $Na_2S_2O_3$ are close to one another, the activity coefficient at 0.1 M, $\gamma = 0.455$, previously assigned to $Na_2S_2O_3$, was also used as a reference value for 0.1 M K_2CrO_4 . The osmotic coefficient of $K_2Cr_2O_7$ has also been evaluated from the above isopiestic data and the results for both salts are given in Table II.

TABLE II.—THERMODYNAMIC PROPERTIES OF POTASSIUM CHROMATE AND DICHROMATE SOLUTIONS AT 25°.

<i>m.</i>	$\phi_{K_2CrO_4}$	$\gamma_{K_2CrO_4}$	$\phi_{K_2Cr_2O_7}$	<i>m.</i>	$\phi_{K_2CrO_4}$	$\gamma_{K_2CrO_4}$
0.1	0.807	0.455	0.868	1.4	0.714	0.214
0.2	0.772	0.379	0.814	1.6	0.717	0.207
0.3	0.753	0.338	0.778	1.8	0.723	0.201
0.4	0.742	0.311	0.752	2.0	0.731	0.197
0.5	0.734	0.292	0.735	2.2	0.742	0.194
0.6	0.727	0.276	—	2.4	0.754	0.193
0.7	0.723	0.263	—	2.6	0.768	0.192
0.8	0.720	0.253	—	2.8	0.782	0.191
0.9	0.717	0.244	—	3.0	0.796	0.191
1.0	0.714	0.236	—	3.2	0.812	0.192
1.2	0.712	0.224	—	3.4	0.829	0.193

The data for the chromate require little comment, save to point out that the osmotic coefficients do not differ from those of $Na_2S_2O_3$ by more than 0.005 at concentrations up to 2 M, nor the activity coefficients by more than 0.003. Thus the changes in the distance of closest approach of the ions, associated with the transitions $Na_2SO_4 \rightarrow Na_2S_2O_3$ and $Na_2SO_4 \rightarrow K_2CrO_4$, are comparable in extent.

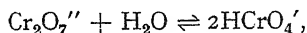
An examination of the data for $K_2Cr_2O_7$ will show that it is difficult to obtain a reasonable extrapolation of either the isopiestic ratio, $2m_{KCl}/3m_{K_2CrO_7}$, or the osmotic coefficient, to the limiting value of unity at infinite dilution. On the contrary, values are obtained for both quantities considerably higher than would be expected on the assumption that the salt is a ternary electrolyte, and the discrepancy increases with increasing dilution. This suggests that a side reaction

³ Robinson and Sinclair, *J. Amer. Chem. Soc.*, 1934, 56, 1830.

⁴ *Ibid.*, 1938, 60, 3061.

⁵ Robinson, *Trans. Faraday Soc.*, 1939, 35, 1217.

intervenes which leads to an increase in the number of ions with increasing dilution of the solution, such as :



with an equilibrium constant :

$$K = \gamma_{\text{Cr}_2\text{O}_7''} \cdot m_{\text{Cr}_2\text{O}_7''} / \gamma_{\text{HCrO}_4'}^2 \cdot m_{\text{HCrO}_4'}^2.$$

An unequivocal test of this hypothesis does not seem to be possible, as the activity coefficient of neither the $\text{Cr}_2\text{O}_7''$ nor the HCrO_4' ion is known as a function of the concentration. Nevertheless, some progress may be made by means of reasonable assumptions. We assume that (1) the calculated vapour pressure lowering of a $\text{K}_2\text{Cr}_2\text{O}_7$ solution in the absence of HCrO_4' ion formation can be taken as that of a K_2SO_4 solution of the same concentration, and (2) the calculated vapour pressure lowering of a $\text{K}_2\text{Cr}_2\text{O}_7$ solution which has been hydrolysed completely to HCrO_4' ions can be taken as that of a KCl solution of twice the molality of the dichromate solution. From the observed vapour pressure lowerings of the dichromate solution it is then possible to derive the degree of hydrolysis, and thence to calculate the equilibrium constant.

Thus, for example, a solution of 0.5 M $\text{K}_2\text{Cr}_2\text{O}_7$ is isopiestic with 0.6135 M KCl and the vapour pressure lowering is 0.4676 mm. A solution of 0.5 M K_2SO_4 has a vapour pressure lowering of 0.4394 mm. and one of 1.0 M KCl has a vapour pressure lowering of 0.7580 mm. We now take the fraction of dichromate hydrolysed as

$$(0.4676 - 0.4394) / (0.7580 - 0.4394) = 0.0885,$$

whence

$$m_{\text{Cr}_2\text{O}_7''} = 0.5 \times 0.9115 = 0.4558 \quad \text{and}$$

$$m_{\text{HCrO}_4'} = 2 \times 0.5 \times 0.0885 = 0.0885,$$

and the total ionic strength is 1.456. The activity coefficients of the $\text{Cr}_2\text{O}_7''$ and HCrO_4' ions at this total ionic strength may be calculated

TABLE III.—APPROXIMATE DATA FOR EQUILIBRIA IN SOLUTIONS OF POTASSIUM DICHROMATE AT 25°.*

<i>m</i> .	<i>α</i> .	<i>m</i> _{Cr₂O₇''}	<i>m</i> _{HCrO₄'}	<i>K</i> .
0.075	76.1	0.0571	0.0358	23.0
0.1	79.4	0.0794	0.0412	22.7
0.15	82.4	0.1236	0.0528	19.6
0.2	84.6	0.1692	0.0616	18.4
0.25	86.3	0.2160	0.0680	18.4
0.3	88.1	0.2643	0.0714	19.6
0.4	90.0	0.3600	0.0800	19.9
0.5	91.2	0.4558	0.0884	19.7

of concordance between values of *K* at different concentrations is moderately good ; it is not affected by the choice of the *ā* value in calculating $\gamma_{\text{Cr}_2\text{O}_7''}$ and $\gamma_{\text{HCrO}_4'}$ because values of 3 and 5 give about the same agreement, although the mean value of *K* does depend on the choice of *ā*. Thus mean values of *K* = 17.8, 20.2 and 22.3 are obtained with *ā* = 3, 4 and 5 Å respectively. Using a value of 4 Å, the "constant"

* *m* = stoichiometric molality of potassium dichromate, *α* = percentage of $\text{Cr}_2\text{O}_7''$ ions not hydrolysed to HCrO_4' ions.

approximately by the Debye-Hückel equations for bi- and uni-valent ions respectively, using a reasonable value of the ionic diameter, *e.g.* 4 Å, but omitting the term linear in the ionic strength. Hence the hydrolysis constant, *K*, may be calculated. Table III gives the results of such calculations at different concentrations. The degree

varies between 18.4 and 23.0, which is not large considering the nature of the approximations which were made in calculating the proportions of $\text{Cr}_2\text{O}_7^{''}$ and HCrO_4' ions present.

Sherrill⁶ determined the depression of the freezing-point of K_2CrO_7 solutions and, from somewhat different considerations, concluded that the equilibrium constant was approximately 61 at the freezing-point.

Summary.

The osmotic and activity coefficients of K_2CrO_4 , determined by the isopiestic method, are very close to those of $\text{Na}_2\text{S}_2\text{O}_8$. This is consistent with the increase of atomic dimensions to be expected for these salts compared with K_2SO_4 and Na_2SO_4 . The osmotic coefficient of K_2CrO_7 is found to be anomalous, and an explanation is advanced in terms of a hydrolysis of the $\text{Cr}_2\text{O}_7^{''}$ ion to the HCrO_4' ion. An approximate value of the equilibrium constant has been calculated.

We are indebted to the Chemical Society for a grant from their Research Fund.

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⁶ *J. Amer. Chem. Soc.*, 1907, **29**, 1641.

THE OSMOTIC AND ACTIVITY COEFFICIENTS OF SILVER NITRATE AT 25°.

BY R. A. ROBINSON AND D. A. TAIT.

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The activity coefficients of potassium, rubidium and caesium nitrate^{1,2} have been found to be small compared with those of the halides and the values for thallous nitrate are even lower. These nitrates, however, form saturated solutions at comparatively low molalities, whereas silver nitrate is saturated only at 14 M at 25°. Some interest, therefore, attaches to isopiestic measurements on solutions of AgNO_3 , and it has now been found possible to make such measurements on this salt up to concentrations of

TABLE I.—CONCENTRATIONS OF ISOPIESTIC SOLUTIONS OF POTASSIUM CHLORIDE AND SILVER NITRATE AT 25°.

Molality.		Molality.		Molality.	
KCl.	AgNO_3 .	KCl.	AgNO_3 .	KCl.	AgNO_3 .
0.1250	0.1297	1.943	3.066	2.984	6.278
0.1771	0.1856	1.958	3.148	3.014	6.393
0.1884	0.1984	1.983	3.208	3.040	6.472
0.2765	0.2958	2.013	3.262	3.160	6.967
0.3303	0.3563	2.026	3.274	3.230	7.180
0.5056	0.5635	2.042	3.359	3.443	8.000
0.6580	0.7620	2.067	3.394	3.693	8.986
0.7755	0.9232	2.076	3.433	3.805	9.467
1.011	1.275	2.108	3.518	3.985	10.18
1.210	1.605	2.371	4.253	4.271	11.25
1.462	2.057	2.464	4.492	4.540	12.41
1.478	2.072	2.494	4.602	4.787	13.38
1.492	2.097	2.528	4.758	4.811	13.48
1.572	2.270	2.677	5.237		
1.582	2.287	2.724	5.385		

¹ Robinson, *J. Amer. Chem. Soc.*, 1935, **57**, 1165.

² *Ibid.*, 1937, **59**, 84.

13.5 M before the solution becomes isopiestic with saturated KCl solution. The isopiestic data are given in Table I, and the osmotic and activity coefficients calculated therefrom are given in Table II.

TABLE II.—OSMOTIC AND ACTIVITY COEFFICIENTS OF SILVER NITRATE AT 25°.

<i>m</i> .	0.1	0.2	0.3	0.4	0.5	0.7	1.0	1.5	2.0
ϕ .	0.902	0.870	0.847	0.827	0.811	0.781	0.744	0.691	0.648
γ .	0.731	0.654	0.603	0.565	0.534	0.483	0.428	0.362	0.315
$\gamma_{\text{calc.}}$	0.730	0.654	0.603	0.565	0.534	0.484	0.429	0.361	0.318
<i>m</i> .	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5
ϕ .	0.611	0.578	0.551	0.525	0.504	0.485	0.469	0.454	0.440
γ .	0.280	0.252	0.229	0.210	0.194	0.181	0.169	0.159	0.150
$\gamma_{\text{calc.}}$	0.281	0.254	0.230	0.211	0.195	0.181	0.170	0.159	0.150
<i>m</i> .	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0
ϕ .	0.428	0.419	0.410	0.402	0.395	0.387	0.380	0.376	0.373
γ .	0.142	0.135	0.129	0.124	0.110	0.114	0.110	0.106	0.102
$\gamma_{\text{calc.}}$	0.142	0.135	0.129	0.123	0.118	0.114	0.110	0.107	0.104
<i>m</i> .	11.5	12.0	12.5	13.0	13.5				
ϕ .	0.368	0.365	0.362	0.358	0.354				
γ .	0.0992	0.0962	0.0934	0.0908	0.0883				
$\gamma_{\text{calc.}}$	0.101	0.098	0.095	0.093	0.091				

$$\log \gamma_{\text{calc.}} = -0.5066 \sqrt{c}/(1 + 0.822 \sqrt{c}) - 0.083c + 0.00395c^2 - \log(1 + 0.036m).$$

Up to about 3 M the activity coefficients of AgNO_3 and RbNO_3 are almost the same. Attention may be drawn to the very low values found in concentrated solution and to the absence of any minimum in the curve of γ against \sqrt{m} .

Table II also contains values of the activity coefficient calculated from a Debye-Hückel equation, using a distance of closest approach of the ions of 2.5 Å. Good agreement with the experimental data is obtained, but only by using a negative coefficient of the term linear in the concentration. The value of the closest distance of approach is below the Bjerrum critical distance and therefore ion-pair formation is to be expected, of the order of 4 % at 0.1 M and 18 % at 1.0 M. Robinson and Davies³ arrived at a similar conclusion for the amount of association in 0.1 M solution from conductivity measurements.

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³ *J. Chem. Soc.*, 1937, 574.

FRACTIONATION AND SIZE DISTRIBUTION IN VINYL ACETATE POLYMERS

By R. A. BLEASE AND R. F. TUCKETT.

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The properties of long-chain molecules are determined by two factors, chemical constitution and molecular length. Hence, the obvious approach to any complete understanding of the properties, both chemical and physical, of macromolecular systems is to isolate these two variables so that their separate effects can be distinguished. This can partly be done in the first place by confining attention to polymers synthesised from the same monomeric unit so that they differ only in the lengths of the chains.

Little work, however, on the variation of physical properties with molecular size has been published, and although there exists a large body of data on the mechanical properties of synthetic polymers, a great deal of it is only comparative and based on empirically developed testing methods which do not give much real insight into the properties of the system: this point has been recently emphasised by Aleksandrov and Lazurkin.¹ For instance, the average stress-strain diagram is of little use in evaluating the properties of a given plastic unless accompanied by some analysis of the deformation at various loads into its ordinary elastic, highly elastic and viscous components.

The concept of molecular size also needs definition. Methods of estimating polymer molecular weights always give an average value, whose magnitude depends on the particular method used. This leads to the familiar distinction between number, weight and Z-average molecular weight:² only when the chains are all of equal length are these quantities the same. To define a given polymer system it is necessary to know not only the average molecular weight (number or weight) but also to have some idea of the non-uniformity of the system. A knowledge of the weight-average chain length (as measured by the empirical Staudinger method) is not enough, and studies of the variation of properties with average particle size, using unfractionated polymers, are apt to give misleading results. This is partly because the degree of non-uniformity increases with the average molecular size for a given series of polymers prepared under similar conditions: this fact arises naturally out of current theories of polymerisation kinetics, as will be shown later. Thus, a high molecular weight polymer will contain a considerable proportion of much smaller molecules and these may well exert a profound effect on some of its properties. This will be especially true if mechanical properties are being studied as the smaller molecules will probably reproduce some of the effects of a plasticiser artificially added.

For the above reasons, any study of the effect of molecular size on physical properties is best done with carefully fractionated samples of

¹ Aleksandrov and Lazurkin, *J. Tech. Phys. (U.S.S.R.)*, 1940, **9**, 1267.

² Lansing and Kraemer, *J.A.C.S.*, 1935, **57**, 1369.

polymers. Very few studies of this kind seem to have been published, the most well known being that of Douglas and Stoops³ on polyvinyl chloride-acetate copolymers. This may partly be due to the fact that the separation of polymers other than polystyrene into bands of different molecular weights has received little systematic study. The results obtained below arose out of some experiments on the fractionation of vinyl acetate polymers, which also gave some information about the size-distribution function in the samples studied.

Experimental.

Polymers in the presence of a solvent can be fractionated either by dissolution or by precipitation.⁴ The latter method is more convenient experimentally, but suffers from the disadvantage that clusters of molecules of different sizes tend to form on adding a precipitant; these then come down "en bloc," thereby ruining the fractionation. This can be avoided to some extent by working in as dilute a solution as is practicable; that this improves the separation has been shown by Douglas and Stoops.³ In the present work an initial concentration of 2 g. of polymer in 100 c.c. of solvent has been used throughout.

In fractionating polymers of styrene and vinyl chloride, suitable control of the experimental conditions makes it possible to bring down the various fractions as fine precipitates which can readily be filtered off. In the case of polyvinyl acetate, however, the fractions are deposited as sticky masses which are not amenable to similar treatment. It is found that these adhere to the sides of the flask on standing, and can be separated from the solution by cautious decantation. To bring about slow precipitation and to avoid high local concentrations, the precipitant is added slowly and with shaking. The solution is then left in a thermostat for at least two days, by which time the supernatant liquid is usually quite clear. After removing as much solution as possible by decantation and draining, the fraction precipitated is dissolved up in acetone and its weight found by evaporating down to constant weight in a conical flask at 90°-95° C. The chain length is then determined by the usual Staudinger method in an Ostwald viscometer (flow time for acetone, 288 sec.) using the levelling precautions recommended by Gee.⁵

This method of separating precipitate and solution is not perfect, as a little unfractionated polymer is always left on the walls after decantation. Blank experiments showed that this is approximately 0.004 g. each time. If the total fraction is comparable with this, a correction can be applied in estimating the chain length, as the mean particle size is known. This has been done where the chain length is high and the weight of the fraction small (~ 0.02 g.)—it can be neglected for large fractions (> 0.1 g.).

As solvent-precipitant mixture, toluene with petrol-ether has been used,⁶ but the high volatility of the latter and the comparatively narrow range in which the fractions come down made it desirable to find some other mixture. The one finally selected was acetone, and 50 % aqueous methanol—the water is the actual precipitant, but if this is used alone accurate control is not easy; the alcohol acts as a diluent, so that the amount of precipitant added can be judged more exactly. Comparative fractionation curves for the two mixtures are given in Fig. 1. In practice, most mixtures can be used for separating polymers of chain length less than 200 units, but the true test of a given mixture is its ability to separate chain lengths of the order 500 units. By this criterion the aqueous

³ Douglas and Stoops, *Ind. Eng. Chem.*, 1936, 28, 1152.

⁴ Bloomfield and Farmer, *Trans. Inst. Rub. Ind.*, 1940, 16, 69.

⁵ Gee, *Trans. Faraday Soc.*, 1940, 36, 1163.

⁶ Shawinigan Ltd., *Private Communication*.

methanol is superior to the petrol ether as precipitant, and the following fractionations were all carried out using this former medium.

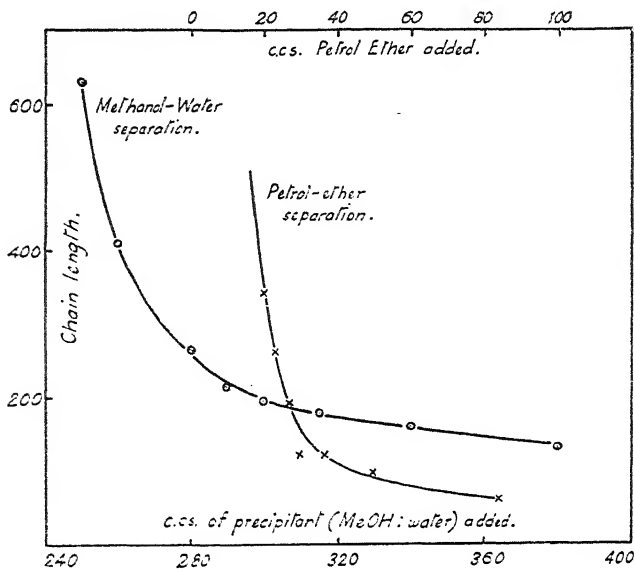


FIG. 1.

The effect of temperature on the degree of separation has also been studied. In general, for a given solvent-precipitant mixture, the solu-

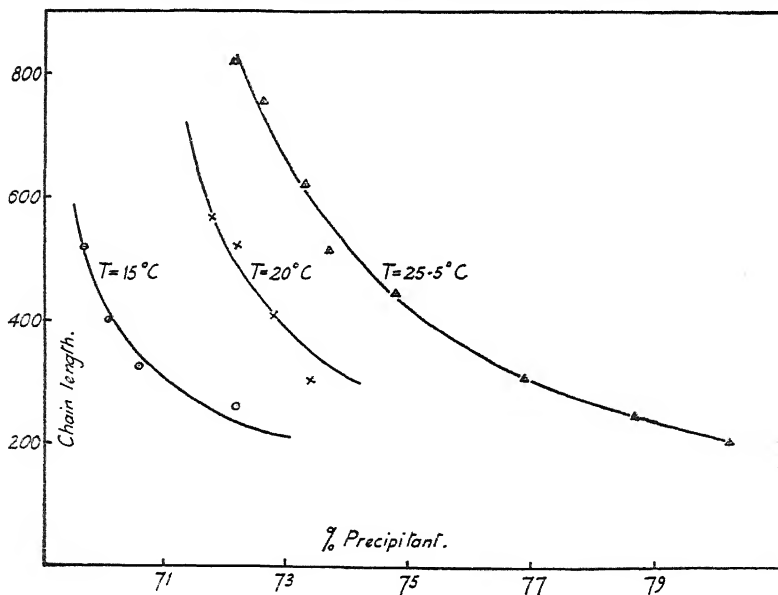


FIG. 2.

bility of a given polymer will increase with the temperature; hence, to bring about precipitation at a given point, it is necessary to add more

precipitant—in effect, this makes the separation easier to control. This is shown in Fig. 2, which gives the fractionation curves at three different

TABLE I.

T (°C.).	Extra Amount of Precipitant (c.c.).
15°	16
20°	23
25.5°	47

temperatures, 15°, 20°, and 25.5° C. To bring down polymers of chain lengths between 300 and 500 the amount of extra precipitant to be added is given by Table I. It is clear that it is advantageous to work at the high temperature to obtain good separation of the higher fractions.

The connection between the size of the polymer precipitated and the composition of the solvent mixture has been considered by Schulz,⁷ following earlier work by Brönsted.⁸ If X is the proportion of precipitant in the mixture, then

$$X = \alpha + \frac{\beta}{P}$$

where P is the degree of polymerisation. For polystyrene, this equation has been shown to hold for precipitation from various solvents.⁹ The results of polyvinyl acetate obtained in the present work agree with this equation, as is seen in Fig. 3.

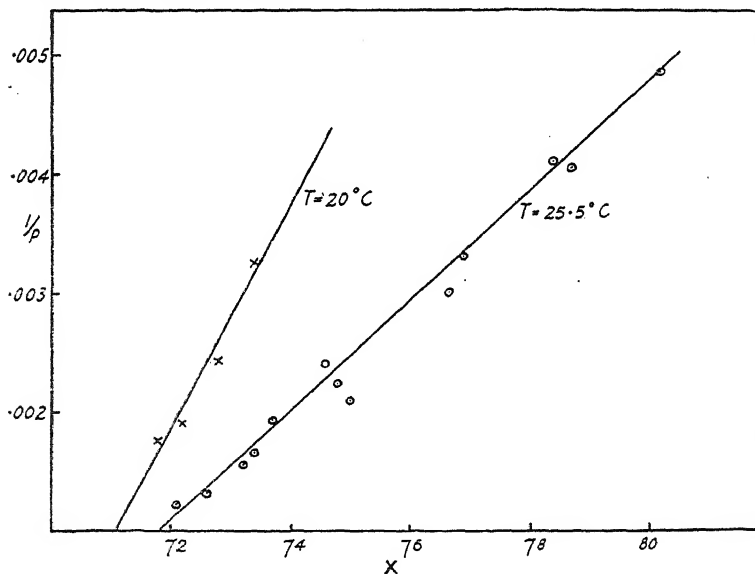


FIG. 3.

Schulz⁷ has also considered the effect of temperature on polymer solubility, and it is interesting to compare his results with the present ones. The solubility C of a polymer is given by

$$C = Ke^{-(A+BX)P/RT},$$

where A , B and K are constants arising out of the theory. From this, X is given by an expression

⁷ Schulz, *Z. physik. Chem.*, A, 1937, 179, 321.

⁸ Brönsted, *Z. physik. Chem.*, Bodenstein Festband, 1931, 22, 99.

⁹ Staudinger and Heuer, *Z. physik. Chem.*, A, 1934, 171, 129.

$$X = \alpha + \psi T$$

$$\alpha = -A/B; \text{ and } \psi = -\frac{R \ln \frac{C}{K}}{BP}.$$

In the case of polystyrene in benzene-methanol mixtures the simple assumption that A , B and K are independent of temperature is not entirely adequate, as Schulz' $X - 1/P$ plots at different temperatures are parallel straight lines; also the $X - 1/T$ plots should give decreasing values of ψ as P increases—experimentally, the lines are parallel. The reasons for the discrepancy are discussed by Schulz. In the case of vinyl acetate, the simple assumption seems to be qualitatively supported as the two $X - 1/P$ lines are not parallel, and moreover give values for α which are independent of temperature within experimental error ($\alpha = 69.6$ and 70.0). Also, the $X - T$ dependency is in accordance with the simple theory as ψ diminishes with increasing P . From the experimental viewpoint, the dependence of the $X - 1/P$ slope on temperature in the present instance is important as the ease of separation is increased by a rise in temperature, unlike the polystyrene fractionation.

Size Distributions.

Very little work has been done on size distributions in polymer systems. In theory, the ultracentrifuge can be used, but the experimental difficulties are considerable, and this method has so far been

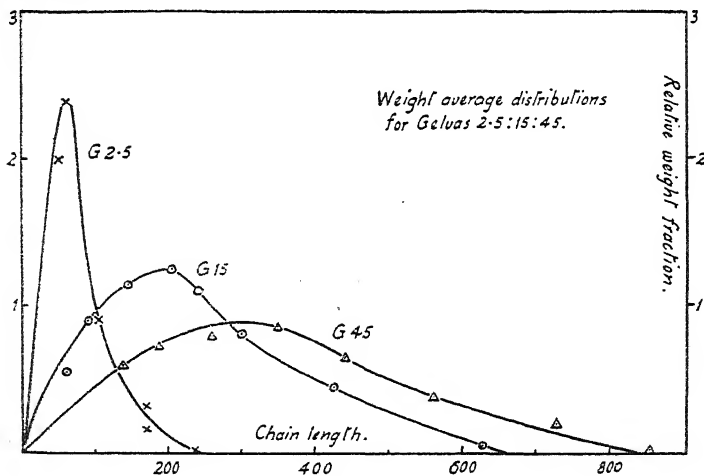


FIG. 4.

used only for one substance, polystyrene:¹⁰ even here, the interpretation of the results has been questioned. A fractional precipitation would seem to be the most direct approach to the problem, and this has been done in the case of polyisobutylene.¹¹ From a given fractionation a polymer is separated into a number of weighed portions of known particle size. To get a size distribution curve from these data, it is necessary to know the width of each polymer band; this is usually a matter of complete guess-work, as the extent to which adjacent bands

¹⁰ Signer and Gross, *Helv. Chim. Acta*, 1934, 17, 59, 335, 726.

¹¹ Schulz, *Z. physik. Chem., B*, 1935, 30, 379.

overlap is not known. It is usually assumed that each fraction is symmetrically distributed about the mean particle weight, and this enables the width of each band to be estimated. The accuracy with which this can be done is the limiting factor in the method. Large errors can partly be avoided by arranging the fractionation so that the various bands are of comparable width; this has been attempted in this case and overlapping of adjacent bands has been neglected. Each polymer has been separated into about six to ten bands, the points at which cuts were made being determined by preliminary experiments.

The polyvinyl acetates used are three technical samples of "Gelvas" (G. 2.5, 15 and 45), kindly supplied by Shawinigan Ltd., whose weight-

average chain lengths are 64, 200 and 328 units respectively. The

$$X - 1/P$$

points for the three polymers (Fig. 3) all lie on the same straight line; thus the molecules of all these polymers probably have the same linear structure, irrespective of size. There is no positive evidence for the existence of branched chains so far; these might be supposed to have different precipitation points for the same Staudinger chain length. One point is still obscure—

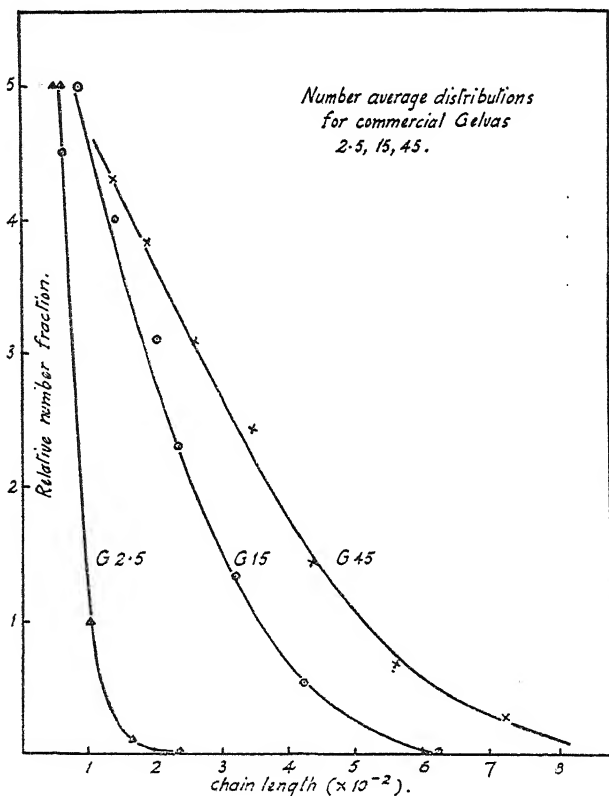


FIG. 5.

although the initial samples are all apparently completely soluble, the first fraction is more like a definite precipitate than succeeding ones, and does not stick to the walls of the vessel; also this fraction (< 1 %) is apparently insoluble in acetone. However, early samples of these resins contained an insoluble portion, but it is stated that this has now been reduced considerably.¹² For chain lengths down to ~ 180 the precipitate used is the aqueous methanol, but pure water has been used to bring down polymers of lower particle size.

¹² E. P. Irany, *Private Communication*.

The final results are shown in Figs. 4 and 5, which show the weight and number fraction plots against chain length for the three samples. (The scales are adjusted to bring out comparative differences.) These show quite clearly that the lower the average molecular weight, the more homogeneous the sample for a series of unfractionated polymers. From the data, both number and weight, average chain lengths can be calculated. These are given by:

$$\text{Number average length} = \nu_n = \frac{\sum_{r=0}^{\infty} r \cdot n(r)}{\sum_{r=0}^{\infty} n(r)}$$

$$\text{Weight average length} = \nu_w = \frac{\sum_{r=0}^{\infty} r^2 n(r)}{\sum_{r=0}^{\infty} r \cdot n(r)}$$

where $n(r)$ is the number of molecules with r units in the chain. For a homogeneous polymer $\nu_n = \nu_w$; for inhomogeneous specimens $\nu_n < \nu_w$, the difference increasing as the degree of non-uniformity becomes larger. The values for the three samples are given in Table II.

The size distribution results can also be used to confirm previous conclusions concerning the mechanism of polymerisation.

A growing polymer chain can be finally terminated in three possible ways:

- (a) By spontaneous deactivation in the gas phase or at the walls. This has not been shown yet to occur for any reaction which has been analysed kinetically.
- (b) By a monomer collision of a different type to that responsible for chain propagation. This is the terminating mechanism in the photochemical polymerisation of acetylene.¹³
- (c) By mutual collision of two growing chains—this is the mechanism most generally encountered.

In vinyl acetate polymerisations, (c) has been shown to be the mechanism, not only in the gas-phase photochemical reaction,¹⁴ but also in the liquid phase and in toluene solution catalysed by benzoyl peroxide.^{15, 16} The latter observation is most relevant, as this is probably the process by which the commercial samples fractionated were made.

To distinguish between the possible termination mechanisms, kinetic methods have been used, but size distribution data can also be applied to a limited extent. The necessary theoretical background has been

TABLE II.

	ν_n	ν_w
G. 2.5	62	68
G. 15	150	203
G. 45	262	328

¹³ Melville, *Trans. Faraday Soc.*, 1936, **32**, 258.

¹⁴ Melville, Jones and Tuckett, *Chem. and Ind.*, 1940, 267.

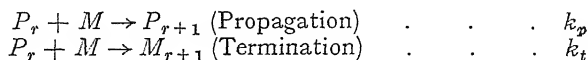
¹⁵ Cuthbertson, Gee and Rideal, *Proc. Roy. Soc., A*, 1939, **170**, 300.

¹⁶ Kamenskaya and Medvedev, *Acta Physicochim. U.R.S.S.*, 1940, **13**, 565.

provided by Melville and Gee.¹⁷ * For monomer termination and photochemical initiation, the number fraction, $n(r)$ of a polymer of chain length r units in a mixture is given by

$$n(r) = \text{const.} \frac{\theta^2}{(1 + \theta)^{r-1}},$$

where θ is the ratio of propagation to termination velocity coefficients, k_p/k_t .



The expression for $n(r)$ does not include any factor depending on the initiation, and so is independent of whether it is photochemical, thermal or catalytic; it can be rewritten in the form

$$\ln . n(r) = a - rb$$

where a and b are constants. Hence the plot of $\ln . n(r)$ against r should be a straight line. On this basis, the data of Schulz on polyisobutylene fractionation¹¹ can be analysed: from the constancy of the mean molecular weight, this author deduces that monomer termination stops the growing chains. That this is not an entirely adequate means of distinguishing this mechanism from others has been pointed out by Breitenbach,¹⁸ who shows that constancy of molecular weight can also be derived under certain conditions with mutual termination. Also Schulz and Husemann, later do not seem to think a constant particle size incompatible with mutual termination,¹⁹ so that the nature of the mechanism in the polyisobutylene case is still open. The relative numbers of molecules in each band are given in Table III, which is calculated from Schulz' results.

TABLE III.

r .	Fraction of Whole.	Estimated Band Width.	Wt. Fraction (Relative).	n_r No. Fraction (Relative).
25	0.035	100	350	1400
295	0.113	275	410	139
600	0.220	300	733	122
950	0.130	400	325	34
1500	0.194	725	268	17.8
2210	0.154	675	228	10.3
2770	0.090	450	200	7.2
3500	0.064	1000	64	1.8

Fig. 6 shows the relation between $\ln . n_r$ and r ; the data are rather inconclusive, but a straight line seems to represent the best fit to the points so that monomer termination here seems to be a more probable mechanism.

Fig. 7 shows the $\ln . n(r) - r$ plot for the two higher fractionated polymers of vinyl acetate. Two definite curves are obtained which

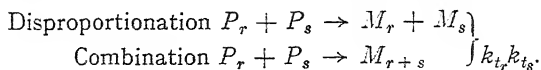
¹⁷ Melville and Gee, *Unpublished Work*.

* We should like to express our thanks to Professor Melville for elucidating some of the points raised in this section.

¹⁸ Breitenbach, *Monat. Chem.*, 1938, **71**, 275.

¹⁹ Schulz and Husemann, *Z. physik. Chem., B*, 1938, **39**, 246.

shows that monomer termination does not occur here. For mutual termination, the theoretical size distributions are more complex, and can only be calculated on the basis of the simplest form of initiation process, *i.e.* photochemical. Even here, there are two possible termination mechanisms involving either disproportionation or combination of the growing chains, and the size distributions for these are not the same.



If I is the rate of photochemical initiation and k_{pr} is the propagation coefficient, the size distributions are given by:

$$\text{Combination.}—n(r) \text{ prop. to } \frac{\delta^2 I}{2(r-1)(r-2)} \left[\left(\frac{r-1}{M_0} + \frac{I}{\delta \sqrt{I}} \right) \left(1 + \frac{\delta \sqrt{I}}{M_0} \right)^{1-r} \right].$$

$$\text{Disproportionation.}—n(r) \text{ prop. to } \frac{\delta I}{(r-1)M_0} \left(1 + \frac{\delta I}{M_0} \right)^{1-r},$$

where $\delta = \frac{\sqrt{k_{tr} k_{ts}}}{k_{pr}}$ and M_0 is the initial monomer concentration.

These can both be written in the form

$$\ln . n(r) = a - rb - \ln . r,$$

so that the $\ln . n(r) - r$ plot is not a straight line but curves down towards the r axis. For more complex forms of initiation, such as catalytic, the size distribution functions cannot be calculated on the basis of the present theory, but may be assumed to be of similar form to the photochemical one with the addition of terms which may or may not be constant. The deviations from linearity in Fig. 7 are in the right direction for mutual termination, so that this is probably the important chain ending process (spontaneous termination also gives a curve for the $\ln . n(r) - r$ plot, but no independent proof of its reality yet exists). Hence

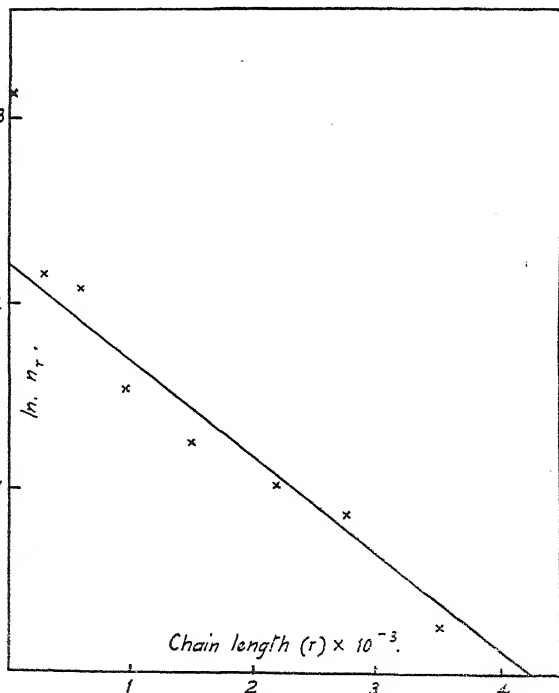


FIG. 6.

in the vinyl acetate polymerisation, both the kinetic and size distribution data are consistent with the view that the chains are terminated by

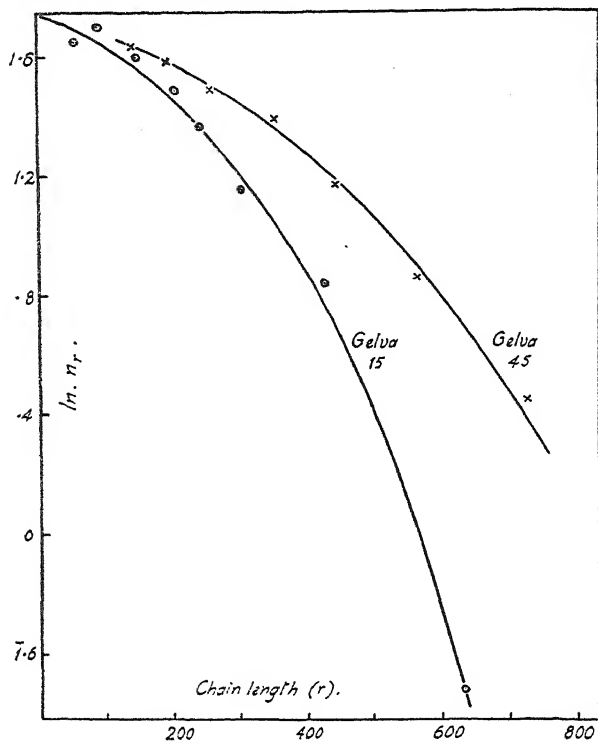


FIG. 7.

mutual collision. The kinetic data on the catalysed styrene polymerisation lead to the same conclusion, and it would be interesting to see if this is confirmed by size distribution data.

It must be emphasised that, in the present state of the theory, size distribution data should only be used to confirm kinetic conclusions so that, although distribution evidence indicates monomer termination in the polyisobutylene case, no more definite conclusion can be stated until kinetic data are available.

Summary.

Commercial polyvinyl acetates of three different average chain lengths have been fractionated from toluene solution by a precipitation method using a methanol-water mixture. The fractionation data have been shown to be in fair agreement with Schulz' theory of the solubility of high molecular weight substances. From the size distribution data obtained in this way combined with the Melville-Gee theory of the kinetics of polymerisation, it is concluded that the growing chains are most probably terminated by mutual collision, in agreement with the purely kinetic data.

We should like to express our thanks to Professor E. K. Rideal for many helpful discussions in the course of this work; one of us (R. A. B.) is also indebted to the Department of Scientific and Industrial Research for financial assistance.

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THE HEATS OF SOLUTION OF MONATOMIC IONS IN METHYL ALCOHOL.

BY D. D. ELEY AND D. C. PEPPER.

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The heat of solution of an ion (or molecule) in a solvent may be evaluated by splitting the process up into two stages.

(1) A cavity the size of the ion is made in the solvent involving the internal energy change ΔE_c .

(2) The ion is removed from the gas phase and placed in the cavity, involving the energy change ΔE_A .

The energy of solution, ΔE° , is then the sum of ΔE_c and ΔE_A . For the solution of gas molecules, where ΔE_A is determined mainly by the London dispersion forces and is therefore relatively small, ΔE_c plays an important part in determining the sign and magnitude of ΔE° .^{1, 2} For the solution of ions in water, where ΔE_A is determined mainly by ion-dipole forces and is relatively large, ΔE_c makes only a small contribution to ΔE° .^{3, 4} Bernal and Fowler,³ in their calculation of the heats of solution of ions in water, divided ΔE_A into three parts.

(a) The energy of interaction between the ion and the water molecules in a first co-ordination shell, one molecule thick. This may be written nP , where n is the number of molecules in this shell, shown by them to be four for the singly-charged monatomic ions.

(b) The energy of interaction between the ion and the rest of the water, which they took as given by the Born equation,⁵ multiplied by an empirical constant. Eley and Evans⁴ have simplified their treatment of this term (neglecting the effect of an intermediate shell of partly saturated dielectric), and use the equation

$$\Delta E_B \cdot c = \frac{Ne^2z^2}{2(r_1 + 2r_s)} \left(1 - \frac{1}{D} \right),$$

where r_1 = radius of ion, $2r_s$ = diameter of solvent molecule, z = number of charges on the ion, and D = dielectric constant of solvent. More strictly, we require Bjerrum's equation,⁶

$$\Delta E_B \cdot c = \frac{Ne^2z^2}{2(r_1 + 2r_s)} \left\{ 1 - \frac{1}{D} - \frac{T}{D^2} \left(\frac{\partial D}{\partial T} \right)_P \right\}.$$

(c) The reorientation energy of the water dipoles in the co-ordination shell of the ion, μ .

Then

$$\Delta E^\circ = \Delta E_c + \mu + \Delta E_B \cdot c + nP.$$

In this way Bernal and Fowler calculate values in good agreement with experiment. Eley and Evans, using a model of the water molecule.

¹ Eley, *Trans. Faraday Soc.*, 1939, **35**, 1281.

² *Ibid.*, 1421.

³ Bernal and Fowler, *J. Chem. Physics*, 1933, **1**, 515.

⁴ Eley and Evans, *Trans. Faraday Soc.*, 1938, **34**, 1093.

⁵ Born, *Z. Physik*, 1920, **1**, 45.

⁶ Bjerrum, *Z. physikal. Chemie*, 1930, **149**, 1.

radii of Sidgwick,⁷ and the charges on the individual atoms were calculated from the bond lengths and the dipole moments given by Eucken

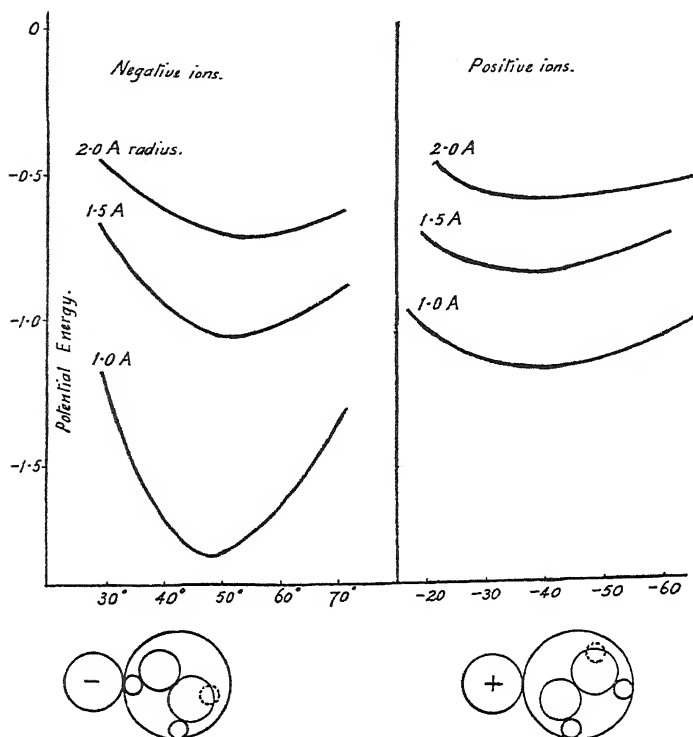


FIG. 2.—Potential curves for the rotation of the CH_3OH in the plane of the paper. The units of energy are 10^{-12} ergs. Underneath is shown the orientation of the alcohol at the position of minimum energy.

and Meyer.⁸ The molecule has been treated as a sphere, which is a rather drastic simplifying approximation, and the energy of interaction between the ion and the alcohol has been considered as purely electrostatic, and calculated by a summation over the six coulombic contributions. The charge separations were measured graphically, the two referring to the H atoms (on the C) out of the plane of the paper being estimated and not actually measured. (This involves only a negligible error in the neighbourhood of the potential minimum.)

TABLE I

Ion.	Radius (Å).	$-4P$ (k.cal.).	$-\Delta E_{B,C}$ (k.cal.).	$-\Delta E^\circ$ (k.cal.).
+	0.78	98.4	37.1	127.5
+	1.0	68.3	35.3	95.6
+	1.5	49.7	32.0	73.9
+	2.0	34.4	29.2	55.6
-	1.0	105.0	35.3	132.3
-	1.5	62.0	32.0	86.0
-	2.0	42.1	29.2	63.3

For an ion of given radius, the interaction energy has been calculated for different

⁷ Sidgwick, *The Covalent Link in Chemistry*.

⁸ Eucken and Meyer, *Physikal. Z.*, 1929, 30, 397.

orientations of the methyl alcohol molecule, so as to obtain the potential minimum, which gives the term P . The orientation is defined by the angle θ between the line of centres of the ion and alcohol, and the C—O axis of the alcohol. In Fig. 2 we show potential curves for the rotation of the alcohol molecule in the plane of the paper, for ions of radius 1.0, 1.5 and 2.0 Å. The values of P for these ions are given in Table I, together with a separate calculation for Li^+ , radius 0.78 Å. In this evaluation of P we neglect repulsive and Van der Waals' forces, which will tend to cancel out but will not completely do so. From this point of view our values of P may be 1 or so k.cal. too high, but the crudity of our model does not justify their consideration.

Energy of the Dielectric.

This we have calculated, using Bjerrum's equation given above. Following Miscenko,⁹ we take $D = 31.5$ and $\left(\frac{\partial D}{\partial T}\right)_p = -0.166$ for methyl alcohol at 25° C. The radius of the alcohol is taken as 1.89 Å. The values of this term used are tabulated in Table I.

Energies of Solution of Univalent Ions.

In Table I we give, for four ionic radii, values of ΔE° calculated by

$$\Delta E^\circ = 8 + \Delta E_B + 4P.$$

These values have been plotted in Fig. 3 and it is now possible to read off values of ΔE° for any actual ion. The radii used are those due to Goldschmidt, as used in the case of water. For comparison with experiment the values for the ion pairs $\text{Na}^+ + \text{Cl}^-$, $\text{K}^+ + \text{Cl}^-$ and $\text{K}^+ + \text{Br}^-$ are taken from Slansky,¹⁰ while the values for $\text{Li}^+ + \text{Cl}^-$ and $\text{Na}^+ + \text{I}^-$ are those quoted by Miscenko. The values are subdivided into the contributions of the separate ions on the basis of the calculated ratio

$$\Delta E^\circ_{\text{K}^+} / \Delta E^\circ_{\text{Cl}^-} = 80/72.$$

For purposes of comparison, we have calculated ΔE° by an application of the Bjerrum equation (see ref. 9), assuming the solvent to be a perfect dielectric up to the surface of the ion (i.e. the radius used in the equation is taken as r_1). These values are to be compared with the values

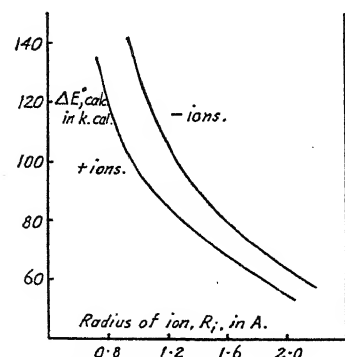


FIG. 3.—The calculated value of ΔE° in k.cal. per mole of ion, as a function of ionic radius, for univalent positive and negative ions.

in the last column, which are the experimental values divided on the basis of the results for K^+ and Cl^- given by this equation. It will be seen that our model gives a much better account of the experimental values, both in regard to the absolute value of ΔE° and the differences between this quantity from one ion to another. Our values are all

⁹ Miscenko, *Acta Physicochemica U.R.S.S.*, 1935, 3, 693. (See also Lange and Miscenko, *Z. physikal. Chemie*, 1930, 149, 1. Askew, Gatty, et al., *J.C.S.*, 1934, 1368.)

¹⁰ Slansky, *J. Amer. Chem. Soc.*, 1940, 62, 2430.

less than the experimental values by an amount 7 to 9 k.cal., which is therefore constant within the accuracy of our methods, while the Bjerrum values show a discrepancy ranging from 71 k.cal. (Li^+) to 22 k.cal. (negative ions). In view of the uncertainty in the evaluation of terms like ΔE_0 and μ we could not expect to obtain the constant term to a better approximation than this, and it is interesting that such a crude model of the alcohol molecule should so faithfully represent the trend in ΔE° over the range of ions.

TABLE II

Ion.	r_1 (Å).	$-\Delta E^\circ$ calc. (k.cal.).	$-\Delta E^\circ$ expt.* (k.cal.).	$-\Delta E^\circ$ (Bjerrum) (k.cal.).	$-\Delta E^\circ$ expt.* (B) (k.cal.).
Li	0.78	128	136.8	216	145.2
Na	0.98	98	106.9	172	115.3
K	1.33	80	88.1	127	96.5
Cl	1.81	72	79.2	93	70.8
Br	1.96	65	72.6	86	64.2
I	2.20	56	63.1	77	54.7

* Strictly these experimental values are ΔH° values, but the difference may be neglected.

The Entropy of Solution.

Latimer and Slansky¹¹ have recently published values for the entropies of solution of the ion-pairs $\text{H}^+ + \text{Cl}^-$, $\text{Na}^+ + \text{Cl}^-$, $\text{K}^+ + \text{Cl}^-$, and $\text{K}^+ + \text{Br}^-$ in methyl alcohol, and divided them on the assumption that \bar{S}° for H^+ (in methyl alcohol) = 0. We give these values in Table III, together with Latimer's earlier values¹² for the entropies of solution of these ions in water, which are again dependent on the assumption that \bar{S}° for H^+ (in water) = 0. In the second case the assumption that $\bar{S}^\circ_{\text{H}} = 0$ is supported by Eastman's determination of $\bar{S}^\circ_{\text{Cl}^-}$, which leads to $\bar{S}^\circ_{\text{H}^+} = -4.6$. The standard states are 1 atmosphere pressure in the gas, and 1 mole per litre in the solution, at 298° K. The entropy of solution is $\Delta S^\circ = \bar{S}^\circ_{\text{soln.}} - \bar{S}^\circ_{\text{gas}}$, the values being in cal. degree⁻¹ mole⁻¹. (Table III).

In the case of water, the simple model already defined gave an equally good account of the entropies of solution as of the energies. It is interesting to observe that this model will not account for the salient facts concerning ΔS° for methyl alcohol. These facts are:

TABLE III

Ion.	$-\Delta S^\circ_{\text{water.}}$	$-\Delta S^\circ_{\text{CH}_3\text{OH.}}$
Na ⁺	20.4	25.4
K ⁺	12.0	25.4
Cl ⁻	22.9	47.4
Br ⁻	19.4	43.4

(a) The difference between ΔS° for K^+ and Cl^- is 22 e.u. in methyl alcohol, while it is only 10.9 e.u. in water. (This difference, of course, depends on the validity of the assumption $\bar{S}^\circ_{\text{H}^+} = 0$ for CH_3OH .)

¹¹ Latimer and Slansky, *J. Amer. Chem. Soc.*, 1940, 62, 2019.

¹² Latimer, Schutz and Hicks, *J. Chem. Physics*, 1934, 2, 82.

(b) The entropy of solution of the ion-pair $K^+ + Cl^-$ in methyl alcohol is 48 e.u. more negative than in water.

At first sight it appeared on the basis of the calculations for water, that (a) might be accounted for by the position of the dipole in methyl alcohol, which is asymmetrically placed relative to the centre of the molecule regarded as a sphere. Actually, the difference in the vibration frequencies is not enough to account for the observed difference. Using potential curves of the type shown in Fig. 1, and assuming, for the purposes of a rough estimate, a similar curve for the libration normal to the plane of the paper, we can write the entropy of libration of 4 solvent molecules as

$$S_{\text{Lib.}} = \text{const.} + 8R \ln \nu_1.$$

A calculation of ν_{K^+} and ν_{Cl^-} , the frequencies of libration, may be made from the appropriate potential curves, and this gives a difference $\Delta S_{\text{Lib.}}$ between the ions K^+ and Cl^- of only 3 e.u. Latimer and Slansky suggest that the positive ions are sufficiently small to fit into cages maintained in the solvent by hydrogen bonds, and that the large negative ions bind unassociated alcohol molecules. This picture would certainly mean that, just as ΔS° is the same for Na^+ and K^+ , so the heats of solution should be the same, which in fact they are not. In connection with point (b), we note that for the solution of gases ΔS° for organic solvents including methyl alcohol, is considerably less negative (about 12 e.u.) than for water. It has already been shown² that this difference arises from the necessity of forming a cavity in the organic solvent, which process results in an increase in the degree of disorder in the surrounding solvent molecules. We can therefore infer that it is necessary to form a cavity, involving a positive entropy (and also energy) contribution, even to dissolve He in methyl alcohol. It would therefore appear that the cavities postulated by Latimer do not exist.

In conclusion we can make one fairly reasonable suggestion, that might account for the more negative entropies in methyl alcohol. If we take the model used for the heats of hydration, we have to consider an ionic solvation shell of four oriented alcohol dipoles. It is a reasonable hypothesis that these dipoles will induce some orientation in a second layer of alcohol molecules; in fact one might expect several layers of more or less oriented dipoles to be formed. Such a structure is not to be regarded as held together by the polarisation force of the ion, which is only appreciable in the first shell. The ion is to be regarded as "seeding" the orientation of the solvent, by forming a first oriented layer. Such a behaviour cannot occur in the solvent water, since the water molecules outside the first shell are held in their normal structure by the strong directed (4-co-ordination) bonds of water. The formation of such layers would add an appreciable negative term to the entropy of solution, but would not be expected to invalidate seriously an application of the Bjerrum equation to the energy of the solvent outside the first shell. This is because such an alteration in the orientation polarisation of the solvent will be reflected in an alteration of $\left(\frac{\partial D}{\partial T}\right)_D$, and therefore in $\Delta S_{B.C.}$ * Alterations in this term of 200%, however, will only affect the value of the energy given by the Bjerrum equation by 10%.

$$* \Delta S_{B.C.} = \frac{NZ^2e^2}{2R} \cdot \frac{1}{D^2} \cdot \left(\frac{\partial D}{\partial T}\right)_D.$$

At the present time there is no direct evidence in favour of the above speculation, although it should be forthcoming from X-ray measurements, of the type carried through so successfully by Stewart¹³ for aqueous solutions. We should note, however, the measurements by Åkerlöf¹⁴ of the activity coefficients of uni-univalent salts in methyl alcohol-water mixtures. At high dilution the Debye-Hückel theory gives $\log \gamma = u\sqrt{2m}$, where m is the concentration of electrolyte. This expression holds both for water and methyl alcohol-water solutions, and it is well-known that in the former the theoretical value of the constant u is obtained. In the alcohol-water solutions the experimental values of u for LiCl, NaCl, and KCl, are much larger than the theoretically predicted values. This might be due to structural modifications of the solvent in some such way as that already suggested.

Summary.

The energies of solution of univalent ions in methyl alcohol have been successfully accounted for by a similar simple model of the ionic solution as was used previously for aqueous solutions. In this model 4 alcohol molecules are assumed to be held in the first co-ordination shell of the ion, and their interaction energy with the ion is obtained by evaluating the electrostatic ion-dipole energy. Outside this first shell the solvent is considered to behave as a perfect dielectric and its energy is calculated by the well-known Born-Bjerrum equation.

A simple explanation of the entropies of solution in methyl alcohol, as compared with water, by a parallel method to the above has failed. A tentative suggestion has been made that the first shell of oriented dipoles can impose a similar orientation over a shell of solvent several molecules thick.

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The University, Cambridge.*

¹³ Stewart, *J. Chem. Physics*, 1939, 7, 869.

¹⁴ Åkerlöf, *J. Amer. Chem. Soc.*, 1930, 52, 2353.

AN ATTEMPTED ISOTOPIC SEPARATION BY FRACTIONAL CRYSTALLISATION.

BY WILLIAM J. C. ORR.

Received 13th August, 1941.

Although the partition ratio of isotopes between two phases in equilibrium seldom differs by more than 0.1 to 0.2 % from unity, progressive concentration can be achieved by continuous fractionation in specially designed columns. Thus Lewis and Macdonald¹ obtained a separation of lithium isotopes, making use of the partition of the lithium ion between two liquid phases. Urey and co-workers² have made a study of a large number of gas-liquid equilibria from this viewpoint, and have designed highly efficient fractionating columns. In view of the relatively greater transport of matter that can be obtained in solid-liquid systems, it seemed desirable to devise a continuous counterflow

¹ Lewis and Macdonald, *J. Amer. Chem. Soc.*, 1936, 58, 2519.

² Urey and co-workers, see H. C. Urey, *Rep. Prog. Physics*, 1939, 6, 48.

method, for crystals in equilibrium with their saturated solution, analogous to those of the above authors. The only measurements extant on the partition of isotopes between crystal and dissolved phase are those of Goldschmidt,³ who examined the distribution after a one-stage crystallisation process of the radio-active isotopes of radium for various radium salts. He obtained no measurable separation within the accuracy of his experimental method which was, however, limited to 1 %. In order to say whether the separation is large enough to be utilised in a fractionating column, an accuracy of 0.1 % would be required. It was

hoped that if the factor was not less than 1.001 to obtain measurable progressive fractionation with the design of column described below.

The object of the present apparatus was to maintain a continuous flow of saturated salt solution (in the present experiments NaCl in an aqueous-alcoholic solution) moving upwards in a long column, while a continuous stream of salt crystals, precipitated from the saturated solution, as it reached the top, passed down the column. The apparatus employed is shown diagrammatically in Fig. 1. The saturated solution of NaCl in a 9 % $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ mixture was circulated

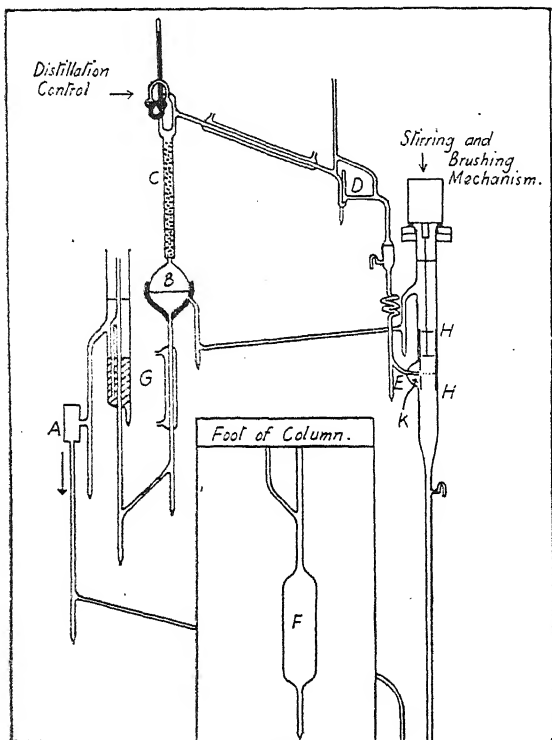


FIG. 1.

ated at a steady rate of 0.16 c.c. per min. by a pump working at A. Alcohol was distilled continuously from the solution at the boiler B (which was electrically heated), and efficiently fractionated by the 60 cm. column C, packed with Fenske⁴ glass spirals, the distillate containing rather less than 1 % water. This alcohol flow was measured at the flowmeter D and automatically controlled at a steady rate of 1.6 c.c. per min. It was the necessity for maintaining the alcohol flow at a rate some ten times greater than that of the main circulation flow which fixed the minimum alcohol concentration which would allow continuous operation at approximately 8.5 % by volume CH_3OH . From the jet E, whose diameter at the orifice was 0.2 mm., the alcohol flowed in an unbroken stream into the centre of the 4 cm. dia-

³ Goldschmidt, *Compt. Rend.*, 1936, 203, 617; 1937, 205, 41; 1938, 206, 1110; *J. Chim. Physique*, 1938, 35, 407.

⁴ Fenske, Tongberg and Quiggle, *Ind. Eng. Chem.*, 1934, 26, 1169.

meter cylindrical precipitation chamber, where mixing and precipitation took place. With the above rates of flow and concentration, every 1 c.c. of saturated solution of 9 % alcohol concentration, became 11 c.c. of 91.7 % alcohol above the jet. Since the NaCl solubilities in these two solutions are 27.5 and 2.0 g. per 100 c.c. respectively, it follows that 20 % of the salt reaching the top of the column was continuously "refluxed." A total of 12.7 g. NaCl passed as crystals down the column to the reservoir F per day. These precipitated crystals were uniformly extremely fine, the bulk having a cube edge of approximately 0.02 mm. Finally, the partially unsaturated solution leaving the boiler B became saturated again at the salt reservoir G and passed thence to the bottom of the column. The column, of pyrex glass tubing, had an internal diameter of 1 cm. and was 13 m. in length between the jet and the reservoir F.

The principal experimental difficulty encountered was that of preventing the growth of crystals round the jet and on the glass above the interface where the liquid from the column and the supernatant alcohol-rich solution met. The following additional details were found necessary:

(1) A close-fitting glass sleeve through which the jet projected only very slightly was inserted at H . . . H to preserve the smooth cylindrical

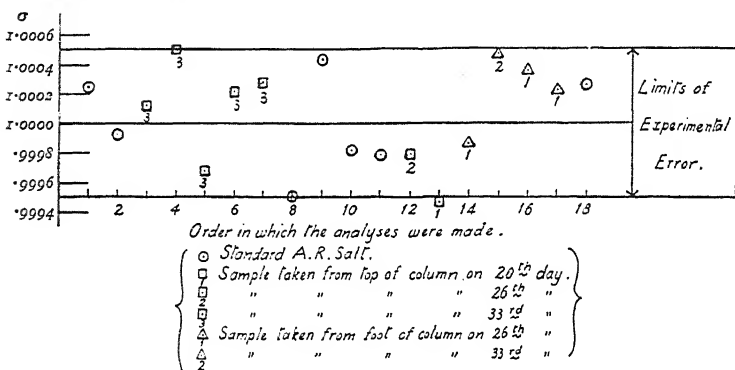


FIG. 2.

contour of the precipitation chamber, and thus prevent the growth of large crystals in such regions as those round the jet at K.

(2) In order to obtain complete mixing in the precipitation chamber stirring at a rate of 3 revs. per min. was necessary. The stirrer consisted of a glass rod shaft, carrying Nichrome wire brushes which lightly swept the cylindrical walls, the lower brush being 4 cm. above the jet. In order to brush away growing crystal nuclei from the tip of the jet and the glass in the interface between the two solutions, it was arranged that the stirrer automatically, at 20 min. intervals, made excursions lasting for 1 min. during which the lower brush swept this region.

The optimum conditions for operation were determined during several lengthy runs. When all the above specified conditions were satisfied, the system worked automatically and continuously without any external attention except the regular replenishing with salt of the reservoir G at daily intervals. In a final completely satisfactory run, which lasted over a period of 1 month, samples of the solution were taken for analysis, at intervals, from the top and bottom of the column.

The analytic method of detecting any change in the atomic weight of chlorine (the only isotopic element present in the system), consisted in comparing the weight of AgCl obtained from given weights of a reference AgNO₃ solution by precipitation with HCl prepared from the test samples of NaCl solution. The AgCl obtained from each sample (about 0.1 g.)

was fused and heated till weighings agreed to the nearest ± 0.03 mg. The experimental error in the ratio,

$$\rho = \frac{\text{Weight of AgCl from sample}}{\text{Weight of reference AgNO}_3 \text{ solution}}$$

should thus not exceed ± 0.05 %. In Fig. 2 are plotted experimental values of the ratio $\sigma = \rho_c/\rho_s$, where ρ_c is the value of ρ obtained with the samples from the column and ρ_s is the average value of ρ determined at frequent intervals during the course of these analyses using samples of the standard A. R. NaCl which was fed into the column at G. It is clear that these results do not differ from the average value for the standard salt by more than the expected experimental error. From this result we conclude that the shift in the atomic weight of chlorine, resulting from one month's continuous operation, was certainly less than 0.05 of an atomic weight unit.

Summary.

The design of a continuous counter flow system to deal with a crystalline phase and its saturated solution, which was developed during an attempt to fractionate isotopes by fractional crystallisation, is described. Using NaCl solutions, no detectable separation of the Cl isotopes was obtained.

The idea of using the above method is due to Dr. J. K. Roberts, under whose supervision this work was carried out. The author gratefully acknowledges the award of a Senior 1851 Exhibition Studentship.

Cambridge.

MIGRATION IN CRYSTAL LATTICES.

By R. M. BARRER.

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Diffusion in solids is amenable to treatments developed in the first place for reaction kinetics. In the latter field two main approaches have been made :

- (i) The Kinetic Theory Method.
- (ii) The Transition State Method.

Early attempts to apply kinetic theory to diffusion in solids were made by Langmuir and Dushman,¹ Bradley,² and Wheeler.³ These attempts were not developed very far. The transition state method was first applied to diffusion in liquids by Eyring,⁴ and to diffusion in solids (organic and inorganic) by Barrer.^{5, 6} Recently Stearn and Eyring,⁷ and Stearn, Irish and Eyring⁸ have made more extensive

¹ Langmuir and Dushman, *Physic. Rev.*, 1922, **20**, 113.

² Bradley, *Trans. Faraday Soc.*, 1937, **33**, 1185.

³ Wheeler, *Trans. Nat. Acad. Sci. India*, 1938, **1**, 333.

⁴ Eyring, *J. Chem. Physics*, 1936, **4**, 283; Eyring and Wynne-Jones, *ibid.*, 1935, **3**, 492.

⁵ Barrer, *Trans. Faraday Soc.*, 1939, **35**, 628, 644.

⁶ Barrer, *Proc. Physic. Soc.*, 1940, **52**, 58.

⁷ Stearn and Eyring, *J. Physic. Chem.*, 1940.

⁸ Stearn, Irish and Eyring, *ibid.*

applications of this method to diffusion in solids and liquids respectively. The present paper, on the other hand, couples the kinetic method to the statistical theory of disorder in crystal lattices, and is an attempt to bring this treatment to as high a stage of development as possible.

Experimental data indicate that one may write $D = D_0 e^{-E/RT}$, where D is the diffusion constant and E the energy of activation for diffusion. The values of E may range⁹ from 8200 to 120,000 cal./mol. for metal-metal diffusion systems; and from 2,260 to 47,200 cal./mol. for diffusion in ionic lattices. The values of D_0 range from 3.5×10^{-9} to 1.0×10^4 cm.² sec.⁻¹ in metals, and from 3.85×10^{-5} to 1.06×10^1 cm.² sec.⁻¹ in salts. A complete theory of diffusion should be able to predict, by calculation, the values both of D_0 and E . Theory has not reached this stage for individual cases. The transition state method can predict a relatively narrow range of values of D_0 ⁷ but is not capable of covering the observed ranges in this constant. The kinetic approach will in this paper be shown to give specific equations for the different possible diffusion mechanisms, and each such equation leads to an appropriate range of values of D_0 . The possible diffusion mechanisms will first be briefly considered.

Models for the Transport of Matter in Solids.

Diffusion may proceed by simple *place exchange* (Fig. 1). The atoms A and B may pass by one another easily only if neighbouring

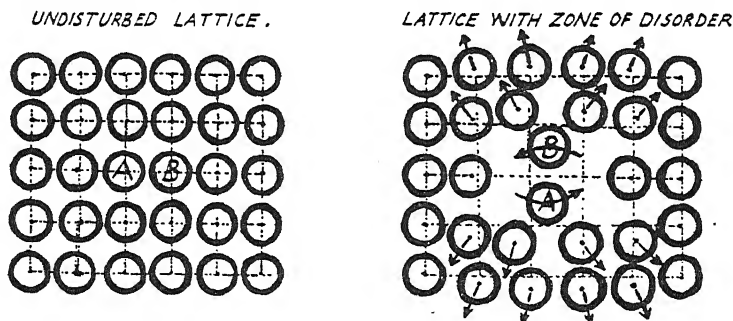


FIG. 1.—Place exchange diffusion, showing zone of disorder produced by vibrations in phase of neighbouring atoms and simultaneous place exchange of A and B made possible by the synchronised vibrations.

atoms move aside simultaneously. Thus diffusion by place exchange requires a local *zone* of disturbance in the lattice.

Crystal analysis indicates that certain aluminosilicates¹⁰ (zeolites, ultramarine, etc.) have channels in the lattice which are sufficiently wide for ions or neutral molecules to diffuse through the structure. Diffusion processes of this kind may be termed *zeolitic*. A variant of zeolitic diffusion occurs in a number of other solid solutions. In these solutions the solute exists interstitially in the solvent lattice.¹¹ This can only happen when the ratio of the atomic radii of solvent to solute

⁹ Barrer, *Diffusion in and through Solids*, Camb. Univ. Press, 1941, Tables 66 and 67.

¹⁰ Cf. Bragg, *Atomic Structure of Minerals*, Oxford Univ. Press, 1937, p. 251 *et seq.*

¹¹ Cf. Evans, *Crystal Chemistry*, Camb. Univ. Press, 1939, p. 146.

is sufficiently small (between 0.23 and 0.59 in various actual crystals). Such a ratio is found when N, C, B, and H dissolve in metals, and diffusion of the solute is then a movement among the interstices.

The study of properties of ionic crystals (conductivity, or uptake of stoichiometric excess of one component has indicated that the crystals may contain centres of disorder. One form of lattice disorder consists in atoms or ions displaced from normal lattice positions. At high temperatures this process may be treated as a chemical equilibrium:

Atoms in Disorder \rightleftharpoons Atoms in their Lattice Sites.

Sometimes the ions may jump from their normal sites to interstitial positions (Frenkel disorder). One may then have two more mechanisms of diffusion:

- (i) diffusion of interstitial ions;
- (ii) diffusion of holes in the crystal lattice.

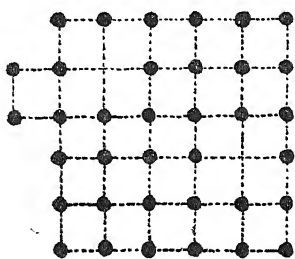


FIG. 2.—Schottky disorder in a two-dimensional lattice.

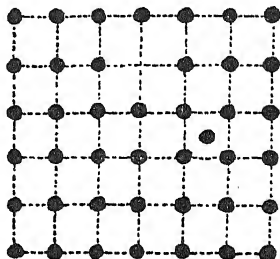


FIG. 3.—Frenkel disorder in a two-dimensional lattice.

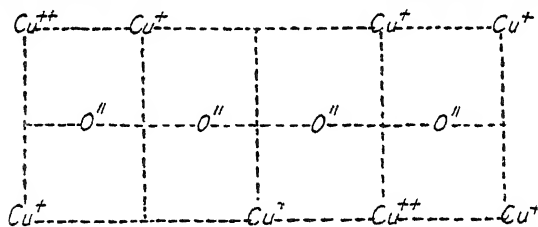


FIG. 4.—Disorder in a lattice of cuprous oxide with stoichiometric excess of oxygen.

A few typical varieties of lattice disorder are indicated in Figs. 2, 3, and 4. Before deducing expressions for the diffusion constants for these mechanisms of diffusion—place change, zeolitic, migration of holes, and migration of interstitial ions—lattice disorder must be briefly but quantitatively discussed.

Equilibrium Disorder in Crystals.

Statistical mechanics applied to Schottky * disorder (Fig. 2) leads to the relation¹²:

$$\frac{n}{N-n} = \alpha_s e^{-W_s/kT} \quad (1)$$

* If ions are displaced from their normal sites, and build up lattice layers on the external surface of the crystal (Fig. 2), they leave holes in the crystal. This type of fault is referred to as Schottky disorder.

¹² Wagner and Schottky, *Z. physik. Chem. B*, 1930, **11**, 163; Mott and Gurney, *Electronic Processes in Ionic Crystals*, Oxford Univ. Press, 1940, Ch. 2.

where n is the number of vacant sites; N , the total number of sites; α_s , a constant; and W_s , the energy needed to create a Schottky defect. The constant α_s arises because the setting up of Schottky disorder causes (i) an increase in volume of the crystal; (ii) a modification of vibration frequencies of the ions round the Schottky defect. An estimation¹³ of α_s suggested that this constant may have values as high as 10^3 to 10^4 .

The statistical treatment of Frenkel disorder (Fig. 2) correspondingly leads¹⁴ to the expression:

$$\frac{n^2}{(N' - n)(N - n)} = \alpha_F^2 e^{-W_F/kT} \quad (2)$$

where n is the number of vacant sites, or interstitial ions; N , the total number of ions; N' , the total number of interstitial ions; α_F , a constant; and W_F , the energy needed to create a Frenkel defect. The constant α_F arises for the same reasons as α_s in equation (1). Its value has been estimated,¹³ and it should be considerably smaller than α_s , and may frequently not differ greatly from unity.

Calculation of the Diffusion Constants.

To avoid complications due to anisotropy it will be convenient first to consider a cubic lattice. It is supposed that the crystal consists of a solution of A in B, and that each atom can diffuse down the appropriate concentration gradient every time it receives the necessary activation energy. The calculation must then be further developed for each diffusion mechanism.

Consider unit area of two neighbouring planes of

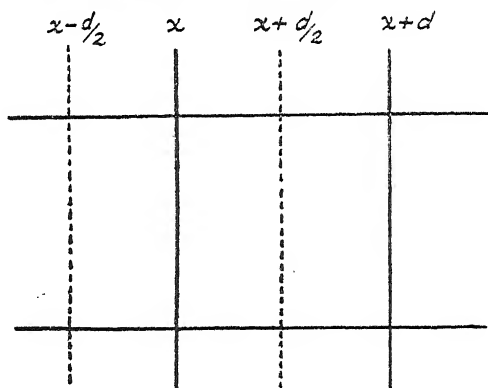


FIG. 5.

atoms in the crystal separated by a distance d (Fig. 5) equal to the interatomic distance. Each atom A when it diffuses moves a distance d in one jump (d = Mean Free Path). Suppose

c = conc. of A in plane x

$c + \frac{\partial c}{\partial x} d$ = conc. of A in plane $x + d$.

All atoms of A in the regions bounded by planes at $x + d/2$ and $x - d/2$ can, if they acquire the necessary activation energy, pass through the plane $x + d/2$. The chance that an activated atom will pass in this direction is $1/6$, for a body-centred cubic lattice, since there are six possible crystallographic directions in which the atom might move, each equally likely. If the vibration frequency is ν , the number of times per sec. that an atom having the necessary E will move in the right direction is

$$1/6 \nu \cdot e^{-E/RT}.$$

¹³ Mott and Gurney, *Electronic Processes in Ionic Crystals*, pp. 29-34.

¹⁴ E.g., Jost, *J. Chem. Physics*, 1933, 1, 466.

The total number of atoms A having both energy and direction suitable for migration in the $+x$ direction is therefore

$$(c \cdot d) \times 1/6 \nu \cdot e^{-E/RT}$$

which equals the (total number of atoms of A in the region between planes at $x = +d/2$ and $x = -d/2$) \times (No. of vibrations having correct direction of vibration) \times (Probability that the atoms have enough energy to move).

In the converse direction the number of atoms A diffusing per second

$$= d \left(c - d \frac{\partial c}{\partial x} \right) \times 1/6 \nu \cdot e^{-E/RT}.$$

The nett transport of A in the $+x$ direction is therefore

$$\begin{aligned} & - D \cdot \frac{\partial c}{\partial x} \quad (\text{Fick's law}) \\ & = - d^2 \cdot \frac{\partial c}{\partial x} \cdot 1/6 \nu \cdot e^{-E/RT} \end{aligned}$$

and thus

$$D = d^2 \cdot 1/6 \nu \cdot e^{-E/RT}. \quad (3)$$

Equation (3), however, assumes that every atom of A which has enough energy to migrate finds a vacant site to migrate into. Equation (3) must be multiplied by the chance of finding a vacant site. This chance is, for *zeolitic* diffusion :

$$\frac{N' - n_1}{N'} = \frac{\text{No. of vacant interstices}}{\text{Total no. of interstices}},$$

where n_1 = the number of occupied interstices.

Further, the equation assumes that the energy of activation for diffusion is accumulated through one internal degree of freedom only. To make the expression general it must be recognised that activation energy may be accumulated through f degrees of freedom. As the final equation one thus has for **Zeolitic Diffusion** :

$$D = d^2 \cdot 1/6 \nu \cdot \left(\frac{E}{RT} \right)^{f-1} \frac{1}{(f-1)!} \frac{N' - n_1}{N'} \cdot e^{-E/RT}. \quad (4)$$

With the **Schottky mechanism** the chance that the atom has a hole adjacent to it is given by

$$\frac{\text{No. of vacant sites}}{\text{Total no. of sites}} = \frac{n}{N}.$$

Allowing in this way for the chance of finding a vacant site, and also for accumulation of activation energy through f degrees of freedom, equation (5) becomes

$$D = d^2 \cdot 1/6 \nu \cdot \left(\frac{E}{RT} \right)^{f-1} \frac{1}{(f-1)!} \cdot \frac{n}{N} \cdot e^{-E/RT}. \quad (5)$$

Remembering that $n \ll N$, and substituting from equation (1) gives

$$D = d^2 \cdot 1/6 \nu \cdot \left(\frac{E}{RT} \right)^{f-1} \frac{1}{(f-1)!} \cdot \alpha_s \cdot e^{-\frac{(NW_s + E)}{RT}}. \quad (6)$$

(where N = Avogadro's number).

For the **Frenkel mechanism** of diffusion, either holes, or interstitial ions, may diffuse, or both. The chance that the diffusing particles

will find holes to move into (which amounts to the oppositely directed diffusion of a hole) is

$$\frac{\text{No. of holes}}{\text{Total no. of sites}} = \frac{\text{No. of interstitial ions}}{\text{Total no. of interstices}} = \frac{n_1}{N}$$

and is given by equation (2). This is also the chance that there is an interstitial ion which can then move according to the mechanism for *dilute* zeolitic solution. In either case, therefore, one finds, by substitution of equation (2), that

$$D = d^2 \cdot 1/6 \nu \cdot \left(\frac{E}{RT} \right)^{f-1} \frac{1}{(f-1)!} \alpha_F \cdot e^{-\frac{(NW_F + 2E)}{2RT}} \quad (7)$$

It must be recognised, however, that each mechanism may have a different E , f , and ν , and that both may occur simultaneously, so that

$$D = D_h + D_i = d^2 \cdot 1/6 \alpha_F \cdot e^{-\frac{NW_F}{2RT}} \left[\nu_h \left(\frac{E_h}{RT} \right)^{(f_1-1)} \frac{1}{(f_1-1)!} e^{-\frac{E_h}{RT}} + \nu_i \left(\frac{E_i}{RT} \right)^{(f_2-1)} \frac{1}{(f_2-1)!} e^{-\frac{E_i}{RT}} \right] \quad (8)$$

One thus notes that when the whole Frenkel defect diffuses in an isotropic crystal it will give rise to a diffusion process dependent exponentially on two temperature factors. Different terms would predominate in different temperature zones, to give the $\log D - 1/T$ curve of Fig. 6. This interpretation may perhaps be applied in some instances where diffusion anisotropy¹⁵ (PbI_2) or where two diffusing atoms or ions¹⁶ have previously been advanced as explanations.

Finally, the **Place Exchange mechanism** must be considered. In this case the movement of the atoms A in the $+x$ direction must occur simultaneously with an equal transport of the atoms B in the $-x$ direction, in order to preserve the crystal lattice (Fig. 1).

The simultaneous movements of A and B may be regarded as having a single activation energy E , but in addition important phase relations have to be fulfilled. At the moment of movement of A there is a movement of B, and a simultaneous displacement of neighbouring atoms to make room for A and B to pass by one another. Each of these atoms, which collectively share in the process, has a chance of moving in any one of a number of preferred crystallographic directions. In the following lattices the number of faces of the polyhedron circumscribing a given atom through which migration is possible is:

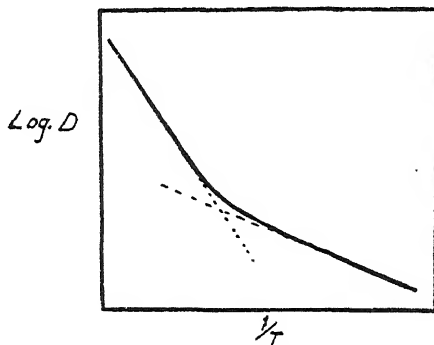


FIG. 6.—The form of the curve of $\log D$ against $1/T$ when
 $D = D_1 e^{-E_1/RT} + D_2 e^{-E_2/RT}$.

¹⁵ Seith, *Z. Elektrochem.*, 1933, 39, 538.

¹⁶ Smekal, *Handbuch. Physik*, 1933, 24, ii, 880.

Cubic close packed . . .	14	6 rectangular and
Hexagonal close packed . . .	14	8 triangular in each *
Body centred cubic . . .	6	
Face centred cubic . . .	8	

Each atom thus has a chance $1/m$ of moving in the correct direction, where m denotes an integer, defined above. If altogether n atoms (including A and B) must simultaneously have the correct phase of vibration for place exchange to occur, the expression for D will become

$$D = d^2\nu \cdot \left(\frac{1}{m}\right)^n \left(\frac{E}{RT}\right)^{f-1} \frac{1}{(f-1)!} e^{-E/RT}. \quad (9)$$

It should be noted that a term $(1/m)^n$ may have to replace the term $\frac{1}{6}$ in equations (3) to (9) to allow for synchronised phase relations and for lattices of other than body-centred cubic symmetry. As a rule, however, phase relations should be simple ($n \sim 1$) for zeolitic, Schottky, and Frenkel mechanisms of diffusion (see later).

Finally, the temperature coefficient of E has been regarded as negligible in the equations (3) to (9), but may actually contribute to the temperature independent terms.² Thus if $E = E_0(1 \pm \alpha T)$, in the term $e^{-E/RT}$, this term reduces to $e^{\pm \alpha/R} e^{-E_0/RT}$, so that $e^{\pm \alpha/R}$ is introduced in the temperature independent terms in equations (3) to (9).

Some Properties of the Diffusion Constants.

It is convenient to represent D by the equation $D = D_0 e^{-E/RT}$. There is a very large range⁹ in the values of D_0 (10^{-9} to 10^4) in the systems studied. The equations (4), (6), (7) and (9) each give different values of D_0 . If we assume a normal vibration frequency in the lattice $\sim 10^{13}$ sec.⁻¹, and a value of $d \sim 3 \times 10^{-8}$ cm., the common term $d^2\nu$ is $\sim 10^{-2}$ cm.² sec.⁻¹. Then the simplest possible model, corresponding to equation (5), gives

$$D = 1/6 \times 10^{-2} e^{-E/RT} \text{ cm.}^2 \text{ sec.}^{-1}. \quad (10)$$

Equation (10) will represent a normal with which the actual behaviour may be compared. This figure for D_0 falls towards the middle of the range of observed D_0 values.⁹

(i) **Zeolitic Diffusion** (eq. (4)) of small interstitial atoms or ions in dilute solution $\left(\frac{N' - n_1}{N'} \sim 1\right)$ can occur according to a clear cut process. The values of D_0 for a number of zeolitic diffusions¹⁷ are:

System	D_0 (cm. ² sec. ⁻¹)
H ₂ —Pd	1.5×10^{-2}
H ₂ —Fc	1.65×10^{-2}
H ₂ —Ni	2.04×10^{-2}
N ₂ —Fe	1.07×10^{-1}
NH ₃ —Analcite	2.5×10^{-3}

These figures are close to the normal for D_0 (see above) of

$$0.17 \times 10^{-2} \text{ cm.}^2 \text{ sec.}^{-1}.$$

* The sets of faces are thus not equivalent. The first preferred would be the rectangular faces, since the interstice is there larger.

¹⁷ Barrer, *Trans. Faraday Soc.*, 1940, **36**, 1235. See also ref. ⁹.

They are all similar in magnitude, and, while more data would be desirable, they suggest that no complicated phase relationships have to be fulfilled (see p. 596 and *cf.* eq. (9)) and that the activation energy is accumulated through only one or two degrees of freedom.

In concentrated zeolitic solutions the value of D_0 will decrease, since then $\frac{N' - n_1}{N'} < 1$. Ultimately, D_0 (and therefore D) tend to zero as the concentration approaches saturation ($\frac{N' - n_1}{N'} \rightarrow 0$). Such a

behaviour has been observed in certain H_2O -zeolite systems as saturation is approached.¹⁸ It is notable that D should be affected primarily through the term D_0 , not through $e^{-E/RT}$, with approach to saturation.

(ii) Schottky Mechanism (eq. (6)).—The migration of an atom into an adjacent hole need involve little disturbance of neighbouring atoms or ions, so that phase relationships as in eq. (9) do not arise. The act of diffusion may proceed with large or small values of f , but, by analogy with zeolitic diffusion where f appears to be small, it is unlikely that activation occurs through many degrees of freedom. On the other hand, the term α_s may have values as high as 10^3 to 10^4 . D_0 for the Schottky mechanism is thus large: $D_0 = 0.17 \times 10^{-2} \times 10^2$, where often $3 < z < 4$.

(iii) The Frenkel Mechanism (eqs. (7) and (8)), whether the diffusion is of holes (Schottky mechanism) or of interstitial ions (zeolitic diffusion) or both, gives for D_0 (*cf.* (i) and (ii)):

$$D_0 \sim 0.17 \times 10^{-2} \alpha_F,$$

where α_F is not very different from unity. When the interstitial ions become too large for the interstices, phase relationships (*cf.* eq. (9)) may be involved. In these conditions, however, Frenkel defects become energetically unstable, and are replaced by Schottky defects.

(iv) Place Exchange Diffusion (eq. (9)) is more difficult to discuss. On the one hand, when f is large, the term $\left(\frac{E}{RT}\right)^{f-1} \frac{1}{(f-1)!}$ has values as high as 10^6 for suitable values of E and T , while on the other hand the term $\left(\frac{1}{m}\right)^n$ is always less than one. In place exchange diffusion D_0 can thus have a range of values, according as phase relationships, or the term $\left(\frac{E}{RT}\right)^{f-1} \frac{1}{(f-1)!}$, predominate.

Metal-Metal Diffusion System.

Metals are in nearly all cases closely packed arrangements of spherical atoms. The predominating structures are cubic close packed, hexagonal close packed, or body centred cubic. These structures have the smallest possible interstitial spaces, and therefore, in an alloy AB, where A and B are of comparable radii, Frenkel disorder and zeolitic solution of A in B or B in A are precluded. The interdiffusion of such metal pairs accordingly conforms to Schottky or place exchange mechanisms.

In a substitutional alloy, where atoms of A increasingly replace those of B in the lattice, as the percentage of A increases, the forces bonding the atoms in the lattice undergo continuous modification. The energy

¹⁸ Tiselius, *Z. physik. Chem. A*, 1934, **169**, 425; 1935, **174**, 401.

¹⁹ Rhines and Mehl, *Trans. Amer. Inst. Min. (Metall.) Engrs.*, 1938, **128**, 185.

needed to create a Schottky defect, and the energy of activation needed for diffusion of the Schottky defect, or for place exchange diffusion, change continuously. By contrast therefore to zeolitic diffusion (p. 596) increasing concentration of solute causes a dominating change* in the term $e^{-E/RT}$ of the equation $D = D_0 e^{-E/RT}$. Fig. 7 shows the change of E with concentration for some interdiffusing metal pairs.

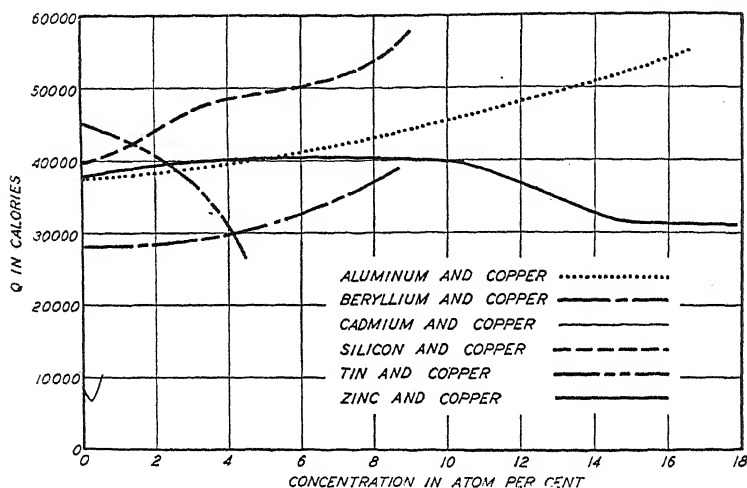


FIG. 7.—Relationship between E and the concentration for the systems Cu-Al, Cu-Be, Cu-Si, Cu-Sn, Cu-Zn (Rhines and Mehl¹⁹).

Diffusion of Salt Pairs.

In ionic lattices the packing density and co-ordination numbers of the ions are usually less than in metals; and one ion (the anion) is frequently much larger than the other (the cation). In such lattices Frenkel disorder is often observed. In a solution of CuI in AgI, for example, we once more anticipate continuous changes in E in the equation $D = D_0 e^{-E/RT}$ for either ion, as the composition alters. Thus Frenkel, Schottky and place exchange mechanisms all differ in this

TABLE I—CONSTANTS IN THE EQUATION

$$K = A_{\text{Cu}^+} e^{-E_1/RT} + A_{\text{Ag}^+} e^{-E_2/RT} \text{ ohm}^{-1} \text{ cm.}^{-1}$$

for CuI—AgI Mixtures.

Composition Mol. % Ag.	A_{Ag^+}	E_{Ag^+} (cal./ion).	A_{Cu^+}	E_{Cu^+} (cal./ion).
100	24.9	4600	—	—
95	36	5400	3.7	5400
90	26	4960	5.7	4960
70	10	3720	8	3720
50	6.3	3270	10.7	3270
30	2.8	2400	11.2	2400
0	—	—	5.5	1190

* There is also a change in the term D_0 , usually such that a small D_0 is associated with a small E . There is no regular functional relation between D_0 and E , however, perhaps in part owing to a lack of highly accurate data.

from the zeolitic mechanism (see p. 596). Table I²⁰ shows these effects for the *conductivity* of CuI—AgI solutions. Conductivity may be regarded as forced diffusion.

Self-Diffusion.

In self-diffusion the migrating atom has the same radius as the lattice atoms; interstitial atoms, for spatial reasons, are then precluded, and Frenkel and zeolitic diffusion are ruled out. In such systems the Schottky or place exchange mechanisms must apply. In the former case large values of D_0 would be expected; in the latter they may also be found. Observation gives for D_0 :⁹

System	D_0 (cm. ² sec. ⁻¹).
Pb in Pb . . .	5.1
Au in Au . . .	1.26×10^2
Cu in Cu . . .	11
Zn in Zn ²¹ . . .	$\sim 1.95 \times 10^{-2}$ *

These figures certainly substantiate the predicted large values of D_0 appropriate to Schottky disorder.

Summary.

Equations have been given for the diffusion constant according to the four mechanisms of migration in solid lattices. These are: zeolitic diffusion, migration of Schottky defects, migration of Frenkel defects, place exchange diffusion.

Simultaneous diffusion of both parts of a complete Frenkel defect gives rise to two exponential terms in the diffusion constant

$$D = D_1 e^{-E_1/RT} + D_2 e^{-E_2/RT}.$$

Migration of half of a Frenkel defect, of Schottky defects, and zeolitic or place exchange diffusion give rise to one only.

The range of theoretical values of the terms D_0 in the equation $D = D_0 e^{-E/RT}$ has been discussed for the four mechanisms, and applied where possible to numerical values. The calculated normal value for D_0 is 1.7×10^{-3} cm.² sec.⁻¹, while the observed values of D_0 range between ca 10^{-9} and 10^4 cm.² sec.⁻¹. Large values of D_0 are to be expected where diffusion is of Schottky defects, or where the activation energy may be accumulated through many degrees of freedom. Small values of D_0 arise when phase relations have to be fulfilled. The range of values observed can be covered by the equations advanced.

In an alloy AB, zeolitic diffusion of A is likely when the ratio of atomic radii A : B is < 0.59 . In solutions of metal pairs of comparable atomic radii diffusion should most frequently be of Schottky defects, or by place exchange. In salt pairs it is usually of Frenkel or Schottky defects.

In a zeolitic solution the terms D and D_0 diminish towards zero at saturation. The value of E need be little affected. On the other hand, changing concentration for the other three mechanisms alters both the terms D_0 and $e^{-E/RT}$.

*The Chemical Laboratories,
The Technical College, Bradford.*

²⁰ Cf. Tubandt, *Z. Electrochem.*, 1933, **39**, 500.

²¹ Banks, *Physic. Rev.*, 1941, **59**, 376.

* This value may need revision when more numerous data are available.

Reports on Progress in Physics. Vol. VII. (London: The Physical Society, 1941.) Pp. 362. 22s. 6d.

The production of this volume, under prevailing conditions, represents a considerable achievement, for the size and form are unchanged and the usefulness and attractiveness which these annual reports have always possessed have been maintained. The usual surveys of progress in such basic subjects as Electricity and Magnetism, Heat and Spectroscopy, which have hitherto appeared year by year are absent from this volume, and apart from reports on Surface Tension and Sound, the book is composed principally of articles on special subjects. A judicious selection of subjects has been made, covering a wide range, and therefore having a wide appeal.

Nuclear processes and reactions again come under review in two useful articles and there is an extensive treatment of electric discharge in gases and its applications which will be welcomed by those whose work lies in this direction. In the domain of physical chemistry, writers from overseas contribute valuable articles on the infra-red spectra of polyatomic molecules, equations of state and substances of high molecular weight in solution. The subject of gaseous films on metals and crystalline solids is one on which a report was perhaps overdue, and it is pleasing to find this among those included in the present volume.

These and other articles which cannot be mentioned individually help to create and to stimulate the interest of the reader who wishes to learn of the progress which has been made in branches of Physics with which he may not be familiar. All the contributors write with authority gained from a first-hand knowledge of their subject, and, in the main, keep in mind the needs of the non-specialist reader. For those who wish to read in greater detail, comprehensive bibliographies are appended.

R. H. H.

CORRIGENDA.

Page 512: Line 1. After first F insert comma and space.

„ 515: At ends of lines 8 and 9 transpose “i” and “l.”

Fig. 2. Curve A is in top left corner.

„ 518: For “Fig. 1a” read “Fig. 1b.”

„ 519: In first formula for “v” and “w” read “V” and “W” respectively.

For “Fig. 1b” read “Fig. 1a.”

In footnote *. For “p. 2” read “p. 509.”

„ 521: Line 2. For “t” read “ \bar{t} .”

„ 548: Line 9. For “Card” read “complete.”

MECHANISM AND CHEMICAL KINETICS OF ORGANIC REACTIONS IN LIQUID SYSTEMS.

A GENERAL DISCUSSION.

Friday, 26th September, 1941.

A GENERAL DISCUSSION of the Faraday Society was held at The Hotel Rembrandt, London, S.W. 7, on Friday, 26th September, 1941, from 10 a.m. to 4.30 p.m. the subject discussed being "The Mechanism and Chemical Kinetics of Organic Reactions in Liquid Systems."

The President, Professor E. K. Rideal, occupied the Chair throughout the meeting. Some 120 members of the Society were present. Luncheon was taken in the Hotel during an interval in the meeting. At the conclusion of the meeting thanks were accorded with acclamation to Professor Emeléus and his colleagues of the Imperial College of Science for providing the epidiascope and other conveniences for the meeting at the hotel, as well as to the authors of the papers which had stimulated so useful a discussion.

The papers submitted in Advance Proof for discussion and the report of the discussion thereon appear in the following pages.

INTRODUCTORY REMARKS.

By C. K. INGOLD.

The Council of the Faraday Society has always shown a remarkable facility for selecting subjects for discussion in so timely a manner that the discussions themselves do not merely record chemical history but make it. We cannot say what degree of usefulness the present discussion will be found to have, but it does seem that, apart from the inevitable limitations imposed by the War, the time for a review of the processes of Organic Chemistry is opportunely chosen.

As everyone knows, the theory of Organic Chemistry underwent its original growth between about 1830 and 1875, and then stagnated for about half a century. In this latter period no general theoretical development took place: ideas of an extremely rudimentary kind concerning structure underwent no refinement; and hardly a beginning was made towards a theory of reactions,—towards the understanding, that is to say, of the processes which organic chemists were using every day for the preparation of new compounds, and generally for the accumulation of a very large body of factual material.

Then, quite recently, and from a historical point of view rather suddenly, the combined work of a few physical chemists and mathematical physicists resulted in the discovery of the physical nature of

chemical combination; and this was a signal, indeed it was a motive and a means, for a scientific revival in Organic Chemistry. A new advance began: for structure was physically intelligible: no longer, therefore, would organic chemists remain ignorant of the processes they employed. Schools of research multiplied, whose clear aim was, and is, to establish Organic Chemistry as a physical science, by elucidating its processes in physical terms, and thus building up a body of theory by means of which those processes can be understood and controlled. It may be several decades before the shape of the attempt can be clearly seen; but a start has been made, a basis given on which the imagination can work.

Therefore the Faraday Society decides to take stock of the position, with the result that we have been presented with an interesting series of papers, concerning which it seems appropriate to make one or two quite general remarks.

I understand that the decision to hold a discussion on this subject was originally taken at the meeting of 1937 in Manchester when reaction kinetics was considered, largely from the point of view of general physical principles. It is interesting to observe the profound effect of that discussion on the present papers, for instance, in the numerous applications which are made of the transition state theory, the usefulness of which was much emphasised in the earlier meeting. Evidently the intention that that meeting should pave the way for this has to a large extent already been fulfilled.

Next, we may note with gratification that all the papers have avoided, on the one hand, the tendency to be observed among physical chemists to drift obscurely into the misty regions of the general theory of reaction rate; and, on the other, the still surviving tendency among organic chemists towards that picturesque but only pseudo-physical type of speculation, which fifteen years ago might have been justifiable, but to-day is an anachronism. This means that the contributors have had before them the ideal of the elevation of Organic Chemistry to a physical status, by the supersession of its old empiricisms and recipes by physical understanding and exact technique. No doubt the same purpose will direct our discussion.

Finally, you will not fail to have observed that more than half the reading matter we are to consider has come from the pens of five distinguished pupils of the late Prof. Kennedy Orton. Those who remember him must well appreciate the enthusiasm with which he would have participated in a discussion, whose motive was his own, and whose official title might appropriately have been applied to his own life's work. A great leader and a pioneer of the movement we are here to further, it is appropriate to notice the large part which, through the first generation of his successors, he has taken in our proceedings.

MECHANISM AND KINETICS OF SUBSTITUTION AT A SATURATED CARBON ATOM.

By E. D. HUGHES.

Received 1st September, 1941.

CONTENTS.

Part I. General Principles.

- (1) Introduction.
- (2) Types of Substitution.
- (3) Duality of Mechanism.
- (4) Mechanism in Relation to the Reactants.
- (5) Mechanism in Relation to the Solvent.
- (6) Determination of Mechanism—Non-solvolytic Reactions.
- (7) Determination of Mechanism—Solvolytic Reactions.

Part II. Special Applications.

- (1) Reactivity of Neopentyl Halides.
- (2) Polyhalogen Compounds.
- (3) Effects due to Carbonyl Groups.
- (4) Effects due to Vinyl and Aryl Groups.
- (5) Effects due to Allyl Groups.
- (6) Application to Anionotropy.

PART I.—GENERAL PRINCIPLES.

(1) Introduction.

Numerous researches on the problem of the reactivity of the alkyl halides and similar organic compounds have been carried out, but, unfortunately, much of the literature on the subject is practically worthless as a contribution to the study of mechanism; for it frequently happens that, even under identical experimental conditions, different members of a series of related compounds may either undergo completely different reactions or participate in a given reaction by different mechanisms. Consequently the results, obtained with neglect of these factors and purporting to represent the relative reactivities of the structures concerned (*e.g.*, the ease of removal of halogen from organic halides), lose much of their significance.

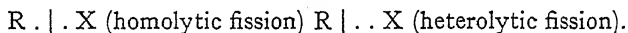
Recent work has sought to remedy this defect; the method adopted combines a somewhat detailed examination of the kinetics of a reaction with a study of the reaction products, and proceeds to compare reaction rates, not only under identical physical condition (with regard to temperature, solvent, reagent, etc.), but also under circumstances leading to a complete uniformity of reaction type and mechanism, as disclosed by the kinetic survey and product analysis. In this way a considerable body of strictly comparable data, relating especially to substitution and elimination reactions, has been accumulated. A similar treatment

has been applied to the study of the stereochemistry of these reactions (particularly of substitution), and one immediate result is that it is now possible to relate the "reactivity" of organic compounds, and the steric course of their reactions, to mechanism and its determining factors, structure and experimental conditions, in a more rational manner than was hitherto possible.* The information thus obtained coheres, and a comprehensive theory of substitution and elimination reactions in aliphatic compounds has been developed.

This paper deals with recent progress along these lines in the field of substitution at a saturated carbon atom. A suitable background is provided by papers contributed to a previous discussion on reaction kinetics.^{1, 2} It will be convenient to review as much as is necessary of the data and of the theory then available (1937), and to proceed with a summary of more recent developments.

(2) Types of Substitution.

In a simple substitution reaction of the form $Y + R-X \rightarrow Y-R + X$, in which only one bond is exchanged ("three-centre system"), it is necessary to distinguish between two main types of bond-fission, *viz.*, symmetric or homolytic fission and dissymmetric or heterolytic fission, defined as follows (the dots representing electrons):³



Processes involving the first type of rupture are common in gas-phase reactions and produce or consume atoms or other neutral particles, while the second form of fission is characteristic of a large proportion of substitution reactions in solution, which generally involve ions, or entities which readily form ions. The substitutions herein discussed are of the latter type, and within this category it is again necessary to distinguish between two forms of "heterolysis," *viz.*, $R | \cdot \cdot X$ and $R \cdot \cdot | X$. Let us suppose that the substitution is to take place at R. Then, which of these two forms will be followed will depend largely on two factors: The first is whether the expelled group (X) tends to separate with its electrons (*e.g.*, chlorine) or without its electrons (*e.g.*, hydrogen), and the second is whether the substituting agent uses its electrons to attack the nucleus of R or uses its nucleus to combine with

* It has often been stated, for instance, that the methyl and *tert.*-butyl halides are very "reactive" in hydrolysis, but it has not always been appreciated that a kinetic qualification should be added to this statement. We now know that the rates of hydrolysis of the methyl halides in dilute alkaline solution are dependent on the alkali concentration, and, anticipating the discussion contained in the following pages, we can state that these halides are highly reactive under conditions favourable to the bimolecular mechanism of nucleophilic substitution (S_N2). In relation to the unimolecular mechanism, which involves a preliminary (rate-determining) ionisation of the halogen (S_N1), they are unreactive. The rates of hydrolysis of the *tert.*-butyl halides, on the other hand, are unaffected by the presence of moderate concentrations of alkali, being the same in acid, neutral and alkaline solution, and these halides are very unreactive towards the bimolecular mechanism (S_N2), but highly reactive with respect to mechanism (S_N1). Furthermore, when a second-order reaction with alkali is realised in the tertiary halides, it leads not to substitution but to elimination (*cf. this vol.*, p. 657). The case of the neopentyl halides (p. 621) provides another good example of the useful application of the kinetic method.

¹ Hughes, *Trans. Faraday Soc.*, 1938, **34**, 185.

² *Ibid.*, p. 202; these papers^{1, 2} contain full references to the original literature.

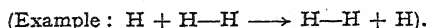
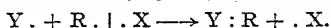
³ *Cf. Ingold, ibid.*, p. 227.

the electrons of R. The former type of substituting agent is termed "nucleophilic" and the latter "electrophilic," and we name the substitution processes accordingly. The classification of substitution processes, so far reached, is illustrated in Table I.*

TABLE I.
FORMS OF SUBSTITUTION.

(A) *Homolytic.*

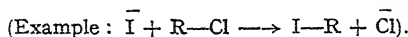
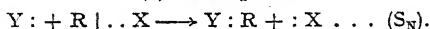
Atomic substituting agent (usual for gas-phase)



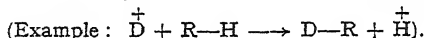
(B) *Heterolytic.*

Ionic or ionogenic substituting agents (usual for solution)

(1) *Nucleophilic.*



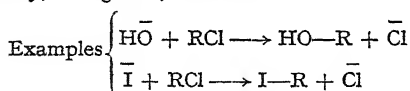
(2) *Electrophilic.*



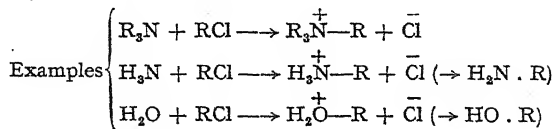
Two forms of heterolytic substitution are therefore recognised, *viz.*, the nucleophilic type (S_N) and the electrophilic type (S_E).⁴ In this report attention will be directed towards the nucleophilic type, and discussion will be restricted to the simplest form, wherein only one bond is exchanged.

TABLE II.
CHARGE DISTRIBUTIONS IN NUCLEOPHILIC SUBSTITUTION.
(Simple type: one bond exchanged.)

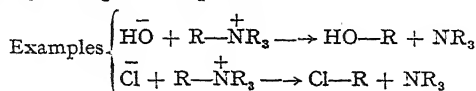
(a) Initially, Y negative, X neutral



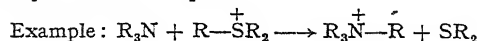
(b) Initially, Y neutral, X neutral



(c) Initially, Y negative, X positive



(d) Initially, Y neutral, X positive



* Each form of substitution is capable of elaboration so that two or even three bonds are exchanged.

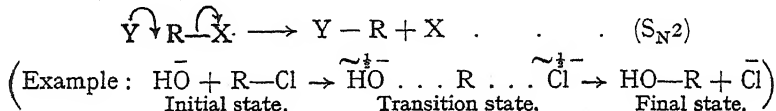
⁴ Hughes and Ingold, *J.C.S.*, 1935, 244.

Within this type of substitution process four cases arise, according to the states of electrification of the substituting agent and the expelled group, as illustrated in Table II.

In nucleophilic substitution, the substituting agent, whatever its original charge, must become one unit more positive, and the expelled group one unit more negative. We obtain four cases, because, initially, the substituting agent may be either negative or neutral, and the replaceable group may be either formally neutral or positive. These variations in charge distributions are responsible for some interesting differences of behaviour,* but this should not obscure the fundamental analogy of the examples.

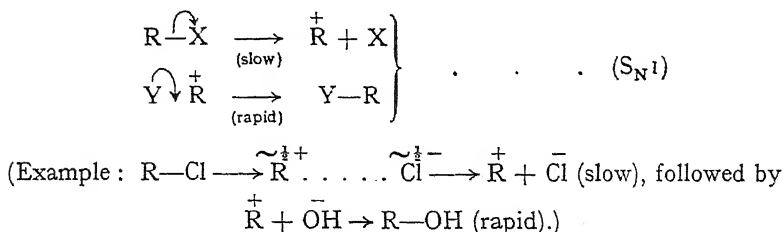
(3) Duality of Mechanism.

In all these heterolytic substitutions in solution there is available a mechanism somewhat analogous to the London-Polanyi-Eyring mechanism of homolytic substitution.† It is a one-stage mechanism, and it is termed "bimolecular," because two molecules are undergoing covalency change:



The main difference from the homolytic case are, firstly, that the existence of charges, in the initial, transition, or final states, give rise to strong solvation forces; and, secondly, that there is an electron transfer from the reagent to the seat of substitution and from the latter to the expelled group. In the transition state, an electron-pair previously unshared in the reagent has become partly shared, and the pair previously shared by the expelled group has become partly unshared.

The known facts relating to the chemistry of the substitution reactions under discussion cannot, however, be explained on the basis of this mechanism alone. There is very strong evidence (*cf.* below) of a second mechanism, proceeding in two stages: a slow ionisation, in which the substituting agent does not take part,‡ is succeeded by a rapid reaction between the formed carbonium ion and the substituting agent:



* *Cf.*, especially, the solvent effect on reaction rate (p. 608).

† The modern view of this type of substitution was first expressed by London (*Z. Electrochem.*, 1929, **35**, 552) in a discussion of the very simplest example of a substitution reaction, *viz.*, the reaction $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$; it envisages a synchronous bond-forming and bond-breaking mechanism, proceeding through a symmetrical transition state, *e.g.* $\text{H} + \text{H}-\text{H} \rightarrow \text{H} \cdots \text{H} \cdots \text{H} \rightarrow \text{H}-\text{H} + \text{H}$.

‡ Except, of course, that, in the case of the solvolytic reactions (p. 611), the substituting agent, which enters stoichiometrically into the subsequent, fast stage, may also constitute the solvating medium for the ionisation.

The rate-controlling ionisation is slow because it has to pass over an energy maximum, which occurs at a certain critical extension of the bond and a certain critical degree of charge-transfer. The energy-maximum is reduced to accessible values by facilitating solvation forces which increase as the charge-transfer increases.* Although the participation of solvent molecules in the transition state of ionisation is recognised, this mechanism is termed the "unimolecular mechanism," because, in the rate-determining stage (the ionisation), only one molecule is undergoing covalency change.†

(4) Mechanism in Relation to the Reactants.

The first indications of the duality of mechanism in nucleophilic substitution were obtained in a study of the hydrolysis of alkyl halides, and of ammonium or sulphonium cations, in alkaline solution (cases (a) and (c), respectively, of Table II). If a series of alkyl groups, or substituted alkyl groups, are placed in order of their ability to release electrons to the centre of substitution, it is found that the rate at first diminishes slowly, whilst the kinetics are of the second order; it then passes through a minimum, in the neighbourhood of which we observe a mixture of second- and first-order kinetics, either of which can be brought into prominence by altering the concentration of hydroxide ions; finally the rate rises very steeply and the kinetics are those of the first order, the rate being quite independent of the hydroxide ions. The hypothesis that the first-order reaction is due to bimolecular substitution with water molecules as reagent (the water being in substantially constant concentration) cannot be upheld, because a nucleophilic substituting agent is acting analogously to a base, and it is inconceivable that water should be so active in this respect, when the much more powerfully basic hydroxide ions are quite inactive.⁴ We suppose, therefore, that, as the electron-releasing capacity of the alkyl group is increased, the bimolecular mechanism of substitution becomes replaced, at first partly, and later wholly, by the unimolecular mechanism.

The rate relationship exhibited is precisely of the type to be expected from a change of mechanism near the point of minimum rate;¹ for groups which supply electrons thereby inhibit the approach of the

* The very large energy required for the formation of gaseous ions is responsible for the circumstance that thermal ionisation does not occur in gas-phase reactions at ordinary temperatures. On the other hand, the spontaneity of ionisation in suitable solutions shows that solvation must reduce the activation energy by an amount which is of the order of magnitude of the bond strength. Those who experience difficulty in accepting ionisation as a mechanism of heterolytic substitution have criticised it on two mutually inconsistent grounds, *inter alia*: (a) that it involves an inaccessibly large critical energy, (b) that, if it occurs at all, it should be practically instantaneous. These are extreme views regarding the magnitude of the critical energy of ionisation, and, between these extremes, we envisage a continuous range, depending on structure and experimental conditions.

† Some authors (*cf.* Steigman and Hammett, *J. Amer. Chem. Soc.*, 1937, 59, 2536) use the term "polymolecular" to signify essentially the same process. We prefer to define molecularity by the number of molecules necessarily involved in covalency change (in the rate-determining process), since the alternative system, strictly applied, would make all reactions in solution polymolecular, the solvent being always present, in principle, at least, in the transition states of reactions in solution (*cf.* Bateman, Church, Hughes, Ingold and Taher, *J.C.S.*, 1940, 1008).

nucleophilic reagent, the presence of which is necessary for reaction by mechanism (S_N2); and they favour the dissociation, which is the rate-determining stage of mechanism (S_N1).

The effect of progressively increasing electron release by alkyl and carboxylate-ion groups (R) on the rate and mechanism of hydrolysis of organic halides (R—Hal.) in dilute alkaline solution is illustrated in Table III (a). Similar results have been established for a series of aryl groups, and for a "mixed" aryl-carboxylate series (Table III (b)), but the rate comparisons have not been so thoroughly investigated in these examples.^{1, 5}

TABLE III.

STRUCTURAL EFFECTS IN NUCLEOPHILIC SUBSTITUTION.

(a) Alkyl and Carboxylate-ion Groups.

Mechanism	S_N2	S_N1
Group (R)	$\begin{Bmatrix} \text{CH}_3 & \text{CH}_2\text{Me} \\ \text{CH}_3 & \text{CH}_2\text{Me} \end{Bmatrix}$	$\begin{Bmatrix} \text{CHMe}_3 & \text{CMe}_3 \\ \text{CHMe}(\text{CO}_2) & \text{CMe}(\text{CO}_2)_2 \end{Bmatrix}$
Reaction Order	2	1
Rate	—decrease→	—increase→

(b) Aryl and Carboxylate-ion Groups.

Mechanism	S_N2	S_N1
Group (R)	$\begin{Bmatrix} \text{CH}_3 & \text{CH}_2\text{Ph} \\ \text{CH}_3 & \text{CH}_2(\text{CO}_2) \end{Bmatrix}$	$\begin{Bmatrix} \text{CHPh}_2 & \text{CPh}_3 \\ \text{CHPh}(\text{CO}_2) & \text{CH}(\text{CO}_2)_2 \end{Bmatrix}$
Reaction Order	2	1

The effect of alkyl substitution is discussed in more detail in the sequel.

Similar evidence of the duality of mechanism has been obtained by effecting changes in the group replaced and in the nucleophilic activity of the reagent.¹

(5) Mechanism in Relation to the Solvent.

The heterolytic substitutions under discussion are characterised by important electrical transferences in the reactant species. The influence of the solvent may therefore be expected to be highly important in these reactions, and, since the effect must depend on the precise manner in which the electrical transferences take place, a change of medium should affect the two mechanisms of nucleophilic substitution (S_N1 and S_N2) both absolutely and relatively to each other. This is found to be the case.

The direction, and, indeed, even a rough idea of the magnitude, of the solvent effect can be obtained by considering the magnitude and distribution of the charges in the transition state of each mechanism in relation to those in the reactants. This has been done for each of the common types of nucleophilic substitutions: by making the plausible assumptions that strongly solvating (ionising) solvents facilitate an increase in the magnitude of the charges, inhibit a decrease, and retard the distribution of a given charge, the direction of the solvent effect was correctly predicted for the several reactions.⁴ A refinement in

⁵ Hughes and Taher, *J.C.S.*, 1940, 956.

the original theory has been introduced⁶ by making the further assumption that a reaction in which the formation of the transition state involves an increase or a decrease in the magnitude of the charges will be subject to stronger solvent influences than one wherein a given charge is distributed in the transition state. The application to the types of nucleophilic substitutions labelled (a), (b) and (c) in Table II (p. 605) is illustrated in Table IV. All these deductions have been tested and all are correct.⁷⁻¹¹

The influence of the solvent in determining the mechanism may be expected to be of most importance in reactions of type (a), in which the direction of the medium effect on rate is different for the two mechanisms, and it is in such reactions that a change of mechanism consequent on a change of solvent was predicted,⁴ and later realised in the example of the meta-hetical reactions of benzhydryl halides with halide ions—which are bimolecular in acetone and unimolecular in liquid sulphur dioxide.¹² *

TABLE IV.
SOLVENT EFFECTS IN NUCLEOPHILIC SUBSTITUTION.

Type and Mechanism.	Charges concerned in Rate-Determining Stage of Reaction.			Effect on Charges of Forming Transition State.		Expected Effect of Ionising Media on Rate.
	Reactants.	Transition State.	Products.	Magnitude.	Distribution.	
1 (a) $\left\{ \begin{matrix} (S_N1) \\ (S_N2) \end{matrix} \right\}$	RX	$\delta^+ R \quad \delta^- X$	$\begin{matrix} + \\ R \end{matrix} + \begin{matrix} - \\ X \end{matrix}$	Increase	—	Strong acceleration
2 $\left\{ \begin{matrix} (S_N1) \\ (S_N2) \end{matrix} \right\}$	$\begin{matrix} - \\ Y \end{matrix} + RX$	$\delta^- Y \quad \delta^- X$	$\begin{matrix} YR \\ + \end{matrix} + \begin{matrix} - \\ X \end{matrix}$	No change	Dispersed	Weak retardation
3 $\left\{ \begin{matrix} (S_N1) \\ (S_N2) \end{matrix} \right\}$	RX	$\delta^+ R \quad \delta^- X$	$\begin{matrix} + \\ R \end{matrix} + \begin{matrix} - \\ X \end{matrix}$	Increase	—	Strong acceleration
4 $\left\{ \begin{matrix} (S_N1) \\ (S_N2) \end{matrix} \right\}$	$\begin{matrix} Y \\ + \end{matrix} + RX$	$\delta^+ Y \quad \delta^- X$	$\begin{matrix} YR \\ + \end{matrix} + \begin{matrix} - \\ X \end{matrix}$	Increase	—	Strong acceleration
5 (c) $\left\{ \begin{matrix} (S_N1) \\ (S_N2) \end{matrix} \right\}$	$\begin{matrix} + \\ RX \end{matrix}$	$\delta^+ R \quad \delta^+ X$	$\begin{matrix} + \\ R \end{matrix} + \begin{matrix} + \\ X \end{matrix}$	No change	Dispersed	Weak retardation
6 $\left\{ \begin{matrix} (S_N1) \\ (S_N2) \end{matrix} \right\}$	$\begin{matrix} - \\ Y \end{matrix} + \begin{matrix} + \\ RX \end{matrix}$	$\delta^- Y \quad \delta^+ X$	$\begin{matrix} YR \\ + \end{matrix} + \begin{matrix} + \\ X \end{matrix}$	Decrease	—	Strong retardation

⁶ Cf. *this vol.*, p. 657.

⁷ Hughes and Ingold, *J.C.S.*, 1933, 1571.

⁸ Gleave, Hughes and Ingold, *ibid.*, 1935, 236.

⁹ Hughes, *ibid.*, p. 225.

¹⁰ Hughes, Ingold and Shapiro, *ibid.*, 1936, 225.

¹¹ Cf. *this paper*, p. 613.

¹² (a) Bateman, Hughes, Ingold, *ibid.*, 1940, 1011; (b) *ibid.*, p. 1017.

* An extension of work in this field has been facilitated by the optical resolution of *m*-chlorobenzhydrol (unpublished experiments by L. C. Bateman and C. T. Ku).

(6) Determination of Mechanism--Non-solvolytic Reactions.

At this stage in the discussion it is convenient to distinguish between two types of nucleophilic substitutions which may be termed "solvolytic"¹³ and "non-solvolytic." It will be seen eventually that there is no essential difference in the chemistry of the two cases, but the technique which has to be adopted in order to establish mechanism is somewhat different.

In the non-solvolytic reactions, several instances of which have already been formulated in the preceding pages (*cf.* Table II), the entering substituent comes from a reagent present in small and controllable concentration. In these circumstances, a bimolecular mechanism normally leads to second-order kinetics, and a unimolecular mechanism to first-order kinetics,* and, in principle, the observed reaction order directly determines the mechanism. Thus the second-order reactions of alkyl halides or 'onium cations with ethoxide or hydroxide ions in alcohol or aqueous alcohol (p. 607), and the similar reactions of alkyl halides with halide ions,¹⁴ or with amines,¹⁵ in solvents such as acetone, are all of the bimolecular, non-solvolytic type. On the other hand, the decomposition of 'onium halides in acetone and similar solvents,¹⁶ the action of water and chloroacetate ions on *tert.*-butyl chloride in formic acid,¹⁷ and the reactions of benzhydryl halides with halide ions, water and amines in liquid sulphur dioxide,¹² are instances of unimolecular non-solvolytic reactions.†

¹³ Steigman and Hammett, *J. Amer. Chem. Soc.*, 1937, 59, 2536.

* This relation between reaction order and mechanism is true only in first approximation, but the deviations, when observable, are of a very characteristic type^{12(b)} (p. 615).

¹⁴ Conant and Kirner, *ibid.*, 1924, 46, 232, and later papers on halogen-exchange reactions.¹

¹⁵ Menshutkin, *Z. physikal. Chem.*, 1890, 5, 589, and numerous subsequent papers by many authors.⁴

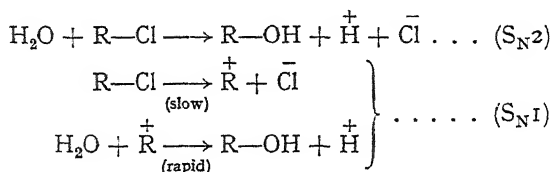
¹⁶ von Halban, *ibid.*, 1909, 67, 129, and others.¹

¹⁷ Bateman and Hughes, *J.C.S.*, 1937, 1187; *ibid.*, 1940, 935; *cf.* Taylor, *ibid.*, 1937, 1852. By way of contrast, the rate of reaction of *n*-butyl bromide with water in formic acid as solvent increases linearly with the water concentration, and added anions produce an acceleration of rate. The reactions of the primary halide, both with water and with anions, are thus bimolecular. There are, however, definite indications of a simultaneous unimolecular reaction, which is slower by a factor of about 10⁸ than the unimolecular hydrolysis of *tert.*-butyl bromide in the same solvent (Bateman and Hughes, *J.C.S.*, 1940, 940). We shall see later that the completely isolated unimolecular reaction of the primary halide, neopentyl bromide, in aqueous ethyl alcohol is also 10⁸ times slower than that of *tert.*-butyl bromide.

† Caution is necessary in the choice of non-reacting solvent for the investigation of, *e.g.*, the hydrolysis of alkyl halides in neutral or acid solution; for, even when there is no stoichiometric intervention by the reagent water in the rate-controlling stage, the addition of comparatively small amounts of a substance, such as water, which as a solvent is very "rapid", to a main solvent, such as acetone or dioxan, which is very "slow," may lead to proportionality between the rate and the water concentration. Thus a unimolecular reaction may have second-order kinetics, just as we have long known that a bimolecular reaction may sometimes have first-order kinetics (Bateman, Cooper and Hughes, *J.C.S.*, 1940, 913; Church and Hughes, *ibid.*, 920; *cf.* Taylor, *ibid.*, 1937, 1853; *J. Amer. Chem. Soc.*, 1938, 60, 2094). It must also be remembered that the mechanism itself may depend on the solvent (*loc. cit.*¹²). The operation of the "mass-law" effect (p. 615) may also, in certain circumstances, introduce new relationships between reaction order and mechanism (*cf.* Bateman, Church, Hughes, Ingold and Taher, *J.C.S.*, 1940, 1003).

(7) Determination of Mechanism—Solvolytic Reactions.

In the solvolytic reactions, which constitute an important class of substitutions (*e.g.*, the hydrolysis or alcoholysis of alkyl halides in neutral or acidic aqueous or alcoholic solvents), the entrant group comes from a relatively large quantity of the solvent, which is present in substantially constant concentration. It is then clear that, in first approximation (*cf.* p. 615), the reaction will be of the first order, independently of whether the mechanism is unimolecular (S_N1) or bimolecular (S_N2), *e.g.*,



This ambiguity has occasioned considerable controversy, and the reactions have been variously described as bimolecular,^{18, 21(b)} as either bimolecular (S_N2) or unimolecular (S_N1) (depending on structure and experimental conditions)¹⁹ and as polymolecular.^{13, 20, 25} We therefore deal with these processes in some detail.

Since the reaction order is no longer diagnostic, a different technique is required in order to establish mechanism in these cases. Several methods have been developed, the first three of which involve a more detailed examination of the structural, reagent and solvent effects already considered in outline. The available methods are listed below and described in this order:

- (i) From the effect of structural changes in the compound substituted on the reaction rate.
- (ii) From the effect of systematic changes in the substituting agent on the reaction rate.
- (iii) From the effect of solvent changes on the reaction rate and on the products.
- (iv) From the stereochemical course of the substitution.
- (v) From the kinetic form of the substitution reaction.
- (vi) From the effect of salt additions on the reaction rate and on the products.

(i) In substitution by nucleophilic reagents, electron-accession to the seat of substitution usually decelerates the bimolecular reaction rather weakly, while it accelerates the unimolecular reaction universally and much more powerfully (p. 607). Exceptions to the stated effect on the bimolecular mechanism sometimes arise, *e.g.*, in the neighbourhood of the bimolecular-unimolecular transition region,¹⁰ but a difference in the magnitude of the effect on the two mechanisms persists even in these circumstances, and the method has wide and useful application.

As a corollary of the principle underlying this method it follows that the occurrence of a rate minimum in a series of groups placed in

¹⁸ (a) Olson and Halford, *J. Amer. Chem. Soc.*, 1937, **59**, 2644; (b) Taylor, *J.C.S.*, 1937, 343, 1962; 1939, 478; (c) Ogg, *J. Amer. Chem. Soc.*, 1939, **41**, 1946; (d) *cf.* Hinshelwood, Laidler and Timm, *J.C.S.*, 1938, 848.

¹⁹ Ingold and Hughes (*loc. cit.*, *cf.* the discussion in the sequel).

²⁰ Farinacci and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 2542; *cf.* however, footnote, p. 619.

order of increasing electron-accession to the centre of substitution, *e.g.*, Me, Et, Pr ^{β} , Bu ^{γ} , may be regarded as an indication (which would require confirmation) of a change of mechanism at, or near, the point of minimum rate. Such a minimum is observed in the solvolytic reactions of the bromides of the above alkyl series in aqueous ethyl alcohol, when "irregular" rate-sequences, *e.g.*, Me > Pr ^{β} > Et < Bu ^{γ} , are obtained ²¹ (the theoretical connection with mechanism in this series is S_N2: Me > Et > Pr ^{β} > Bu ^{γ} and S_N1: Me < Et < Pr ^{β} < Bu ^{γ}). The detailed rate relationships suggested that the reaction may be bimolecular for MeBr, essentially so for EtBr, partly so for Pr ^{β} Br, and essentially unimolecular for Bu ^{γ} Br, and the results of the application of other mechanistic criteria for solvolytic reactions (below) were entirely consistent with this view.

(ii) The second mechanistic criterion depends on the effect on reaction rate of changes in the reagent, and especially on the action, or absence of action, of reagents which are much more strongly acidic or basic than the solvent. As already stated (p. 607), if these powerful reagents do not influence the rate, it is inconceivable that the solvent should function as a reagent in the rate-determining process. If, on the other hand, such extraneous reagents do affect the rate, it means that they participate in the incursion of a bimolecular reaction, but it requires further consideration to determine whether or not the same is true of the reaction with the solvent. The somewhat detailed analysis then necessary in order to obtain an answer, which, admittedly, is rather less convincing in these circumstances, is best illustrated by its application to the solvolytic reactions of the bromides of the alkyl series, Me, Et, Pr ^{β} , Bu ^{γ} , in aqueous ethyl alcohol. In this example the effect of adding sodium hydroxide to the solvent was investigated; the relevant data ^{21(a)} are assembled in Table V.

TABLE V.

RATES OF SUBSTITUTION OF ALKYL BROMIDES IN 80 % AQUEOUS ETHYL ALCOHOL AT 55°.

k_1 = first-order constant in sec.⁻¹; k_2 = second-order constant in sec.⁻¹ g.-mol.⁻¹ l.

Alkyl Halide.	10 ⁵ k_1 (obs.) (First-order Solvolytic Reaction).	10 ⁵ k_2 (obs.) (Second-order Reaction with NaOH).	10 ⁵ k_1 (calc.) (Total reaction, [NaOH] = 1).
MeBr . . .	0.349	2140	2140
EtBr . . .	0.139	171	171
Pr ^{β} Br . . .	0.237	4.75	4.99
Bu ^{γ} Br . . .	1010	—	1010

If we imagine the sodium hydroxide concentration to be buffered to N., the second column figures become first-order constants under the mass-law, and the total reaction can be represented by constants which are numerically the sum of the two, as is shown in the last column of figures. Comparing these totals with their components, we find pure second-order reactions for MeBr and EtBr, a reaction predominantly of second order

²¹ (a) Bateman, Cooper, Hughes and Ingold, *J.C.S.*, 1940, 925; (b) *cf.* Taylor, *ibid.*, 1937, 992; 1938, 840; 1939, 1872.

for Pr^βBr , and a negligible second-order reaction for $\text{Bu}^\gamma\text{Br}$. Taking account of the concentration of the solvent for the purpose of an order-of-magnitude calculation, it is found that the specific rate which would have to represent the activity of water and alcohol in the assumed bimolecular reaction with methyl and ethyl bromides is about 10^{-5} times smaller than the corresponding rate for the reaction with hydroxide and ethoxide ions, and this is quite consistent with the known relationships between specific rates and basic strengths (Brönsted). In the case of *isopropyl* bromide, however, a partly unimolecular reaction seems to be indicated by a rate ratio which is only of the order 10^{-2} - 10^{-3} ; whilst for *tert.*-butyl bromide the absence of a measurable second-order reaction with sodium hydroxide shows the solvent reaction to be essentially unimolecular. Incidentally, it will be observed that the second-order (bimolecular) rate constants (second-column figures) decrease from methyl to *tert.*-butyl (as theory predicts, *cf.* method (i)).

(iii) The evidence to be obtained from the effect of solvent variation is not qualitatively diagnostic, for theory requires (*cf.* Table IV, cases 3 and 4) that a change to a more highly solvating solvent should increase the rate both of the unimolecular process and of the bimolecular reaction with the solvent; quite unlike the bimolecular reaction with anions, the rate of which is decreased (case 2). We find, however, that the incipient charges in the transition state of the bimolecular reaction (case 4) are more widely distributed than those of the unimolecular transition state (case 3), and it is reasonable to expect a stronger solvation, and therefore a larger increase of rate consequent upon a change to a more highly solvating solvent, in the latter than in the former. It is therefore of interest to compare the effect of solvent variation on the solvolytic reactions of the bromides of the alkyl series, Me, Et, Pr^β , Bu^γ , for which the two foregoing tests indicated a change of mechanism. The data show²¹ that, while the rates of all the reactions of the series are increased by changing to a more highly solvating solvent, the effect is very large for *tert.*-butyl bromide, considerably smaller for *isopropyl* bromide, and still smaller for methyl and ethyl bromides. The evidence so far discussed therefore coheres in assigning a change of mechanism in the solvolytic reactions of these halides. There is also some indication that, as we change from less ionising to more ionising solvents, the unimolecular mechanism, which depends on ionisation, gains in relative importance. This being so, we should find that the point of minimum rate, which was observed in the solvolytic reactions of the alkyl halides under discussion, and provisionally associated with a change of mechanism (*cf.* method (i)), should shift to the left in the series, Me, Et, Pr^β , Bu^γ , as we increase the ionising capacity of the solvent. Consistently, in weakly aqueous acetone the minimum is found at Pr^β (observed sequence: $\text{Me} > \text{Et} > \text{Pr}^\beta < \text{Bu}^\gamma$), in strongly aqueous alcohol it is found at Et (observed sequence: $\text{Me} > \text{Et} < \text{Pr}^\beta < \text{Bu}^\gamma$), while in aqueous formic acid it shifts to Me (observed sequence: $\text{Me} < \text{Et} < \text{Pr}^\beta < \text{Bu}^\gamma$).^{21, 22} In aqueous formic acid the theoretical rate sequence for the unimolecular mechanism is therefore fully realised.

The effect of solvent variation has also been utilised to establish mechanism in a somewhat different way, which involves a comparison of rates and product compositions for a solvolytic reaction in a mixed solvent, both components of which may enter into the reaction. The

²² Bateman and Hughes, *J.C.S.*, 1940, 945.

method has been illustrated with respect to the simultaneous hydrolysis and alcoholysis of *tert.*-butyl chloride in aqueous alcohol. The rate of the total first-order reaction of this halide (hydrolysis plus alcoholysis) is very markedly increased by increasing the water content of the solvent.⁹ With reference to the effect of such variations of solvent composition, Olson and Halford^{18(a)} examined the applicability of an equation in constructing which they assumed the reaction to be bimolecular: $\text{Rate} = (k_a p_a + k_w p_w) p_{\text{RCl}}$, where k_a and k_w are specific rate constants for pure alcohol and pure water, and p_a , p_w and p_{RCl} are the partial vapour pressures of alcohol, water and *tert.*-butyl chloride, respectively. The formula may be used either to calculate the total rate or, from the partial rates $k_a p_a p_{\text{RCl}}$ and $k_w p_w p_{\text{RCl}}$, to deduce the composition of the product (*tert.*-butyl alkyl ether and *tert.*-butyl alcohol). Having determined the constants k_a and k_w from the observed rates at two extremes of solvent composition, the authors showed that the rate-interpolation formula worked extremely well, and concluded that the reaction was indeed bimolecular.

It was pointed out by Bateman, Hughes and Ingold,^{23(a)} however, that the success with which the formula describes the rate variation owes nothing to the assumed mechanism, and that the essential requirement, in order to derive conclusions relative to mechanism, was to ascertain whether the measured specific rate constants, which are successful in the rate interpolation, also serve to calculate the composition of the product. This composition should be correctly calculated with the aid of these constants if the products are formed in the reaction stage whose rate is measured (*i.e.*, if the reaction is really bimolecular), but not if rates and products are determined in different reaction stages, as in the unimolecular mechanism. In the case considered the observed proportions of ether were far larger (2.3 times) than the proportions calculated on the basis of Olson and Halford's treatment, and similar discrepancies had already appeared in the work of Farinacci and Hammett in the analogous example of benzhydryl chloride.^{20, 23(b)} It was therefore concluded that the solvolysis of *tert.*-butyl and benzhydryl chlorides under these conditions does not take place by the one-stage bimolecular mechanism. The results are, however, consistent with the two-stage unimolecular mechanism, which requires no direct connection between reaction rates and product compositions.

We are not here concerned with the reasons why Olson and Halford's treatment is successful in giving a reasonably accurate description of the variation of total rate with solvent composition, when it is known that the activity-rate theory lacks general validity. This point has been discussed by Bartlett,²⁴ who also concluded that the results do not support a bimolecular mechanism, but are entirely consistent with the unimolecular mechanism. It has been suggested²⁵ that Olson and Halford's rate formula should be applied on the basis of an assumed one-stage termolecular or quadrimolecular mechanism, involving two or three solvent molecules in the transition state of reaction. It is claimed that this proposal brings rates and product compositions into harmony (in the case of *tert.*-butyl chloride). It is pointed out,²⁶ however, that the approximate agreement obtained between theory and experi-

²³ (a) *J.C.S.*, 1938, 881; (b) *cf.* Bateman, Hughes and Ingold, *J. Amer. Chem. Soc.*, 1938, 60, 3080.

²⁴ *Ibid.*, 1939, 61, 1630.

²⁵ Winstein, *ibid.*, p. 1635.

²⁶ Bateman, Church, Hughes, Ingold and Taher, *J.C.S.*, 1940, 1009.

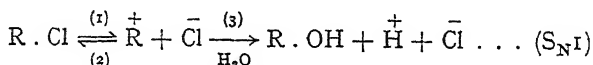
ment is of little significance in view of the paucity of data and the latitude which the method allows in the selection of the several additional constants now introduced.

By way of contrast with the above results, it has been shown that in the solvolysis of *n*-butyl bromide in aqueous-alcoholic solvents (for which other indications point to a bimolecular mechanism), the Olson-Halford equation can be applied to the calculation of both total rates and product compositions.²⁷

(iv) The stereochemical method is described only in outline, since a survey of data relating to the steric course of substitution was included in a previous discussion.² It depends essentially on the circumstance that substitution by the bimolecular mechanism (S_N2) invariably leads to inversion of configuration, while the unimolecular mechanism may give rise, depending on structural influences, either to retention of configuration or to racemisation with a predominating inversion. Thus α -bromopropionic acid and its methyl ester exhibit quantitative inversion of configuration in their solvent reactions, and it was concluded, mainly on this account, that these reactions are bimolecular.²⁸

(v), (vi) These two closely related methods, depending on the kinetic form of the substitution reaction (v), and the effect of added salts (vi), have but recently been developed in detail.^{29, 30}

The application of the direct kinetic method (v) is possible because the statement that the bimolecular and the unimolecular mechanisms require essentially first-order kinetics for solvolytic reactions is substantially true only for bimolecular substitution (S_N2); for unimolecular substitution (S_N1) it is only true as a limit, from which large deviations of a highly characteristic nature may arise. Consider the unimolecular hydrolysis of an alkyl chloride in an aqueous solvent, a reaction for which it is easy to choose conditions such that the complete substitution is experimentally irreversible. The component processes being labelled (1), (2) and (3) as follows:—



the previously stated condition for first-order kinetics was $k_1 \ll k_3$,^{1*} where the rate constants are related to the instantaneous rates, v_1 , v_2 and v_3 , of the stages of mechanism S_N1 by the equations

$$v_1 = k_1[RCI], v_2 = k_2[R^+][Cl^-] \text{ and } v_3 = k_3[R^+].$$

There is, however, a second condition; for, with $k_1 \ll k_3$ only the observed rate is $v_1 v_3 / (v_2 + v_3)$ and this leads to a complicated rate-law which reduces to the first-order law, corresponding to the rate of ionisation ($v = v_1 = k_1$

²⁷ Unpublished experiments by Dr. M. L. Bird.

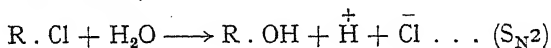
²⁸ Cowdrey, Hughes and Ingold, *J.C.S.*, 1937, 1208.

²⁹ (a) Bateman, Hughes and Ingold, *ibid.*, 1940, 960; *ibid.*, p. 974; Church, Hughes and Ingold, *ibid.*, 966; Church, Hughes, Ingold and Taher, *ibid.*, 971; (b) Bateman, Church, Hughes, Ingold and Taher, *ibid.*, 979. The data recorded in these papers refer to the hydrolysis, in various acetone-water mixtures, of certain alkyl halides for which there were previous indications of a unimolecular mechanism.

³⁰ Unpublished work by E. C. Bloor and R. Percy on the hydrolysis, in acetone-water mixtures, of *n*-butyl halides—structures favourable to the bimolecular mechanism.

* In the pre-prints this condition was formulated as $v_1 \ll v_3$, and the author is indebted to Dr. E. A. Guggenheim for drawing attention to the error.

[RCl]), only if, in addition, $v_2 \ll v_3$. In certain cases the second condition may be fulfilled; in general, however, it is not, and the deviations from the first-order kinetic form then provide a highly distinctive criterion for the unimolecular mechanism. The nature of these deviations can be predicted quantitatively by application of the mass-law. Qualitatively, we can see that, as larger concentrations of chloride ions are built up by the progress of reaction, the rate v_2 will increase, the fraction $v_3/(v_2 + v_3)$ will thereby decrease, and the observed rate will decrease progressively below the first-order rate of ionisation (v_1). Accordingly, the calculated first-order rate constants should diminish with the progress of reaction, and they should diminish in a calculable manner. This characteristic deviation from first-order kinetics has been observed; in suitably chosen examples it was large enough to change the kinetic form completely. Furthermore, the detected disturbance has been shown to be quantitatively in accord with the requirements of the unimolecular mechanism.²⁹ This effect obviously does not apply to the one-stage bimolecular mechanism,



and this is also in agreement with observation.³⁰

The development of method (vi) is based on quite analogous considerations. There are three principal cases to be considered: (a) The simplest effect arises from the addition of a salt (*e.g.*, NaCl) whose anion is identical with that formed from the alkyl halide (*e.g.*, RCl); in this case the rate of the reaction, from its commencement onwards, may be decreased in the unimolecular mechanism. This distinctive effect has been realised.²⁹ The bimolecular mechanism provides for no such retardation in irreversible hydrolysis, and no effect of this kind has been observed amongst reactions regarded for other reasons as bimolecular.³⁰ (b) In the second case, the anion of the added salt (*e.g.*, NaBr) is such that the alkyl derivative which it might form (*e.g.*, RBr) is much more rapidly hydrolysed than the original alkyl halide (*e.g.*, RCl). In the unimolecular mechanism the initial rate should now be unchanged, and the growing retardation discussed in the preceding paragraph should be decreased. The bimolecular mechanism, however, requires acceleration throughout the course of reaction, the acceleration depending directly on the extent to which the added anion attacks the alkyl halide molecule. (c) In the third case the anion of the added salt (*e.g.*, NaN_3) is such that the corresponding alkyl derivative (*e.g.*, RN_3) is not hydrolysed. The conclusions concerning the total rate of destruction of the alkyl halide (*e.g.*, RCl) are the same as in the preceding case. However, there are now two final products (*e.g.*, ROH and RN_3), and the correlation of their proportions with the rate changes provides a further test of mechanism, the principle involved being the same as that discussed in the description of method (iii). In the one-stage bimolecular mechanism there should be a definite and simple relation between the proportions of products and the measured (total) rate, while in the two-stage unimolecular mechanism no such relation is to be expected. A further criterion can be based on a comparison of the proportions of products as between one halide and another. If two different alkyl halides have the same alkyl group, the unimolecular mechanism requires that the proportions in which the products are formed should be the same, because the products are formed from a

common intermediate cation. According to the bimolecular mechanism, we should not necessarily expect any connection. All the deductions relating to the unimolecular mechanism, arising from the application of conditions (b) and (c), have again been realised,²⁹ while uncompleted experiments have provided a preliminary check on the deductions concerning the bimolecular mechanism.³⁰ The qualitative effects, together with those arising from changes of ionic strength (below), are summarised in Table VI, where the term "specific rate" is used to denote the instantaneous first-order rate constant, *viz.*, $(dx/dt)/(a-x)$.

The effects just described may be referred to as "mass-law effects" characteristic of the unimolecular mechanism. They are the most important and distinctive cause of deviation from first-order kinetics, but not the only cause, since account must be taken of "ionic strength effects," *i.e.*, effects arising from the electrostatic interaction of charges. These effects are small for the bimolecular mechanism, but in the unimolecular mechanism they are quite large. It has been shown, however, both theoretically and practically that this universal disturbance is qualitatively opposite to the special deviation, relating to the unimolecular mechanism, which derives from the mass-law when the limiting situation, represented by $v_2 \ll v_3$, does not obtain.

The qualitative picture of the ionic strength effect is very similar to that by which the solvent effect is explained (p. 608). In both the unimolecular ionisation of an alkyl halide and its bimolecular reaction with a solvent molecule, there is a partial separation of charges in the transition state; this will therefore be stabilised (and its energy reduced) by the interaction of these charges with the ionic atmosphere, just as it is stabilised by their interaction with solvent dipoles. The effect of increasing the ionic strength will thus parallel the effect of changing to a more highly solvating solvent; the rate of both reactions (bimolecular and unimolecular) will be increased,* but, because the bimolecular transition state is characterised by a greater diffusion of the incipient charges, the ionic strength effect on the bimolecular mechanism, like the solvent effect, will be smaller. Since the ionic strength increases in the course of a solvolytic substitution of an alkyl halide, the ionic strength effect should lead to calculated first-order constants which rise with progress of reaction. Moreover, the whole rate should be increased by this effect if we add initially either an ionised chloride, or any other ionised salt. These statements will apply to both the unimolecular and the bimolecular mechanisms, the only difference being that the former should be much more sensitive. The effects, which have been observed experimentally,^{29, 30} are summarised in Table VI.

By making a calculation of the interaction energy between the central dipole in the transition state of the unimolecular mechanism, and the surrounding ions, similar to Debye's calculation for the interaction energy between a central ion and surrounding ions, it can be shown that, in dilute solution, the ionic strength effect should increase the rate of the unimolecular reaction by the factor $e^{\text{const. } \mu/D^2T^2}$, where μ is the ionic strength, D the dielectric constant of the solvent, and T the absolute temperature; even the constant, which depends on the constitution of the alkyl halide, can be calculated from the Morse

* As expected, the ionic strength effect on the bimolecular reaction with a solvent molecule is quite unlike that relating to the bimolecular reaction with anions, the rate of which is decreased by increasing ionic strength (*cf.* Beste and Hammett, *J. Amer. Chem. Soc.*, 1940, 62, 2481).

function with a fair degree of approximation for molecules which are not too complicated.^{29(b)} The effect of increased ionic strength should therefore cause calculated first-order rate constants to rise in accordance with the factor stated. Furthermore, since the whole effect depends

TABLE VI. IONIC STRENGTH AND MASS-LAW EFFECTS IN NUCLEOPHILIC SUBSTITUTION.			
Mechanism.	Method.	Ionic Strength Effect.	Mass-Law Effect.
(S _N 1)	(5) Kinetic form (6) Salt effects	Progressive rise of specific rate Acceleration	Progressive fall of specific rate {Retardation ("common-ion" salts) No effect * (other salts)}
(S _N 2)	(5) Kinetic form (6) Salt effects	Small progressive rise of specific rate Small acceleration	No effect {No effect ("common-ion" salts) Acceleration † (other salts)}

* No effect initially; the subsequent "progressive fall of specific rate," due to the mass-law effect of the liberated halide ions, is, however, modified by other ions.

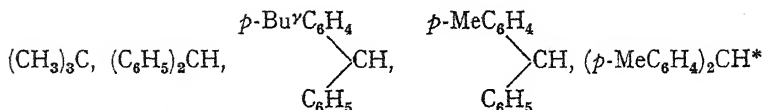
† This acceleration must agree with the product composition when the product given by intervention of the added salt is stable.

on the solvent only through its dielectric constant, the ionic strength effect should change with solvent variation in a calculable manner. These quantitative relationships have been investigated, and the observations are in good agreement with theory, both absolutely and in relation to the dependence of the effect on solvent composition.²⁹

For the sake of simplicity in the description, the mass-law and ionic strength effects have been treated as if they were separate, while, in actual cases, they are, of course, often superposed (*cf.* Table VI). This happens, in particular, in those instances of unimolecular reactions in which there is an appreciable departure from the limiting situation, $v_2 \ll v_3$, and, even more particularly, in relation to the kinetic form of the solvolytic reactions, and the effect of "common-ion" salts, in these examples. The special mass-law effect is, under these circumstances, superposed on the universal ionic strength effect of opposite sign, and the situation could best be analysed by examining the reactions of a series of those alkyl halides which, on less direct evidence, were previously thought to be of the unimolecular type.²⁹ Amongst these, it was possible to indicate in advance the types for which the mass-law disturbance should be weakest

and the type for which it should be strongest.* The mass-law effect should, for example, increase from left to right in the alkyl series,

* The rule is that the effect should increase with the stability of the organic cation; the longer the time interval between the consecutive stages of the unimolecular substitution the more pronounced should be the mass-law effect.



This was found to be the case, and the investigation of the left-hand members gave the ionic strength effects in their most nearly pure form, thus establishing a basis from which the superposed mass-law effects could be assessed when towards the right-hand end of the series they make the dominating contribution.†

In the investigation,²⁹ the main results of which are summarised above, evidence was obtained concerning the molecularity of the two rapid processes which may be involved in hydrolysis by the unimolecular mechanism, *viz.*, the ionic recombination and the hydroxylation of the cation (processes (2) and (3), p. 615). The ionic recombination is unimolecular with respect to each of the participating ions, while the hydroxylation is unimolecular with respect to the alkyl cation and multimolecular with respect to water. The former result is obviously to be expected; the latter result is also reasonable, because many solvent molecules must be involved in the solvation shell of the alkyl cation, and the subsequent reaction of this system need not depend on an extraneous water molecule, the system itself containing all the necessary factors for its own destruction.

The ionic strength and mass-law effects, characteristic of the unimolecular mechanism, were also observed in the non-solvolytic reaction of fluoride ions with *m*-chlorobenzhydryl chloride in liquid sulphur dioxide.^{12(b)} This reaction follows no simple kinetic order, but it exhibits the distinctive kinetics of the unimolecular mechanism. The ionic strength effect, which is observed without interference from the mass-law effect by studying the variation of initial rate with fluoride-ion concentration, is unusually large in this instance, partly because the reaction is unimolecular and partly because the dielectric constant of sulphur dioxide is rather small. The effect is of the calculated magnitude, and its dependence on concentration in dilute solution accurately follows the e^- -law deduced for an ionisation (p. 617). The mass-law effect is also very large. It entirely controls the kinetic form of substitution, since the ionic strength does not change in the course of reaction. The same effect, superposed on, but completely dominating, the ionic-strength effect is apparent in the influence of initially added chloride ions on the initial reaction rate.‡

* The cationic stability in such a series can be roughly correlated with the rate of hydrolysis by the unimolecular mechanism (which increases from left to right), and there are other reasons for placing the groups in this serial order.²⁹

† Hammett had criticised the ionisation mechanism on the grounds that the "mass-law" effect was never observed in solvolytic substitutions¹³ (*cf.* Hammett, *Physical Organic Chemistry*, McGraw Hill Book Co., Inc., New York, N.Y., 1940, p. 172). However, the operation of this effect, first announced by Bateman, Hughes and Ingold in 1938 (*J. Amer. Chem. Soc.*, **60**, 3080) and fully demonstrated in the papers²⁹ now reviewed, has since been confirmed by Beste and Hammett (in the hydrolysis of benzyl chloride in aqueous dioxane; *J. Amer. Chem. Soc.*, 1940, **62**, 2481), who state that it lends strong support to the ionisation theory. Substantial agreement in views is therefore restored.

‡ In a recent investigation, Bartlett and Nebel (*J. Amer. Chem. Soc.*, 1940, **62**, 1345) observed simultaneous second- and third-order kinetics in the reaction of *p*-methoxybenzhydryl chloride with low concentrations of methyl alcohol in nitrobenzene, buffered to definite concentrations of chloride ions. The authors concluded, on this basis, that simultaneous bi- and tri-molecular reactions

Summarising this section, we may state categorically that the duality of mechanism has been demonstrated for both solvolytic and non-solvolytic reactions.* There is, in fact, no essential difference between the two types, the distinction made being one of convenience rather than of actual behaviour. Refined kinetic analysis can deal with both classes, and the evidence of mechanism is parallel, and equally significant.

PART II.—SPECIAL APPLICATIONS.

In Part I we reviewed the phenomena which led to the idea of duality of mechanism in nucleophilic substitution, the factors which determine mechanism, and the methods available for recognising each particular mechanism. We now proceed to discuss the application of these principles to certain special problems.

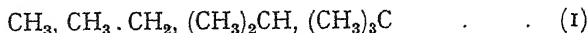
(1) Reactivity of Neopentyl Halides.

Recent work on the substitution reactions of the alkyl halides has sought to provide comparable kinetic data which take account of

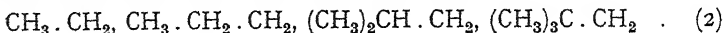
were involved, and that the results supported Hammett's polymolecular mechanism. It was pointed out,^{29(b)} however, that the treatment neglects the importance of the mass-law effect, and that the observations relating to the kinetic order are, under the circumstances, equivocal indications of mechanism. To avoid confusion it should also be stated that the authors' use of the term bimolecular in this connection is quite different from ours. We employ this nomenclature to signify the one-stage substitution process, involving attack by the nucleophilic reagent (in this instance a methyl alcohol molecule) on the carbon of the carbon-halogen bond (S_N2), whereas Bartlett and Nebel are referring to an attraction between a methyl alcohol molecule and the halogen, in what apparently constitutes the first stage of a reaction mechanism approximating to our two-stage mechanism. In accordance with our practice of defining molecularity by the number of molecules undergoing covalency change in the rate-determining process, we designate this mechanism the "unimolecular mechanism" (of nucleophilic substitution, S_N1), and refer to a selective attraction for halogen, such as that pictured by Bartlett and Nebel, as electrophilic catalysis, since the substituting agent and the substitution process (completed later) are still nucleophilic (*cf.* Bateman, Cooper, Hughes and Ingold, *J.C.S.*, 1940, 925).

* In view of this conclusion, it is necessary to examine the evidence underlying Ogg's assertion that the unimolecular mechanism does not exist.^{18(c)} This author claims to have established by calculation that the activation energies demanded by the unimolecular mechanism would be at least 50 Cal., and therefore much too great to admit of measurable rates at ordinary temperatures. His calculations, however, apply primarily to the reactions of the methyl halides in water, and, as repeatedly stated in papers from these laboratories (*cf.* above), these structures are most unsuitable for the operation of the ionisation mechanism (*cf.* Bartlett and Knox, *J. Amer. Chem. Soc.*, 1939, 61, 3184). It was pointed out moreover (Bateman, Church, Hughes, Ingold and Taher, *J.C.S.*, 1940, 1006) that the calculations are, in any case, too rough to signify, the uncertainties introduced being of the same order of magnitude as the quantities calculated. It is thus of interest to note that Baughan, Evans and Polanyi (*Trans. Faraday Soc.*, 1941, 37, 377) have recently arrived at a much lower value (~ 30 Cal.) for the activation energy of the ionisation of methyl iodide in water—a value which would accommodate an ionisation mechanism even for this halide. It would seem therefore that Ogg's "unequivocal decision as to the mechanism of methyl halide hydrolysis" (*loc. cit.*) is founded on an insecure basis; so also, *a fortiori*, is his more sweeping suggestion that ionisation mechanisms "must be abandoned."

mechanism. The effect of the progressive replacement of α -hydrogen by methyl in the series,



was one of the first problems to be examined from this point of view, but the effect of β -methyl substitution, in the series,



has not hitherto been fully investigated.

Before the time of our kinetic investigation of series (1) it had often been remarked that the last member of the series was very "reactive" in hydrolysis, but this statement, taking no account of mechanism, left vague the question of what reagent *tert.*-butyl halides were supposed to be reactive towards; hydroxide ions are usually thought of in connection with the hydrolysis of alkyl halides. Kinetic investigation showed, however, that *tert.*-butyl halides are unreactive to hydroxide ions though they are highly reactive to water. To-day a somewhat similar situation prevails with regard to series (2). The common assertion now is that the last member of the series is extremely unreactive. Again, however, we shall show that a mechanistic qualification is necessary, since neopentyl halides have a moderate reactivity to water, although they are singularly insensitive to alkalis.*

A kinetic investigation of the substitution reactions of the halides of series (2), with special reference to the neopentyl compounds, has been carried out in these laboratories. The principal reactions examined are those of the bromides, (a) with sodium ethoxide in dry ethyl alcohol, and (b) with "50 % " aqueous ethyl alcohol in initially neutral solution. We have supplemented these measurements by a parallel examination of the reactions with silver nitrate in "70 % " aqueous ethyl alcohol (c). The data for this complicated reaction, which involves heterogeneous catalysis by precipitated silver halide,³¹ are of dubious value in connection with rate comparisons of this type, but they provide a check on certain points. The main results for the bimolecular reaction with sodium ethoxide are summarised in Table VII, and the relative rates ($\text{Et} = 1$) for all three reactions are listed in Table VIII. A satisfactory discussion of the problem involves a comparison with the corresponding reactions of methyl bromide, and this also appears in the Tables.

The most important point which emerges from this comparison is that the large decrease in reactivity associated with the neopentyl halide is shown most forcibly in the reaction with sodium ethoxide—a reaction which, throughout the series, is of the second order, and evidently bimolecular (S_N2). The rate relationships for the first four members are fairly normal for the bimolecular mechanism, the rate of which is decreased by electron-accession to the reaction centre (*cf.* Part I), but the introduction of the last β -methyl substituent has obviously introduced an effect which is far larger than that to be expected on the basis of its capacity for the release of electrons. The type of

* The only reliable information concerning the properties of the neopentyl halides comes from the work of Whitmore and his co-workers (*cf.* especially, Whitmore and Fleming, *J. Amer. Chem. Soc.*, 1933, 55, 4161; Whitmore, Wittle and Popkin, *ibid.*, 1939, 61, 1586).

³¹ Hughes, Ingold and Masterman, *J.C.S.*, 1937, 1236; Cowdrey, Hughes and Ingold, *ibid.*, 1243.

variation exhibited cannot be explained by postulating a facilitating electromeric polarisation, $\text{H}-\text{C}=\text{C}-\text{Br}$, which decreases as the β -

TABLE VII.

BIMOLECULAR RATES FOR THE REACTIONS OF PRIMARY HALIDES WITH SODIUM ETHOXIDE IN DRY ETHYL ALCOHOL.

k_2 = second-order constant in $\text{sec.}^{-1} \text{ g.-mol.}^{-1} \text{ l.}$

Bromide.	Methyl.	Ethyl.	n-Propyl.	isoButyl.	Neopentyl.
$10^3 k_2^{55^\circ}$	$\sim 25^*$	1.97^{32}	0.547^\dagger	0.058^\dagger	—
$10^3 k_2^{95^\circ}$	—	76.6^\ddagger	—	—	$0.00050^{33} \S$

* Estimated from experiments in "80 %" aqueous ethyl alcohol.²¹

† Unpublished experiments by M. L. Dhar and S. Masterman.

‡ Calculated from experiments at lower temperatures.³⁴

§ It has been shown³⁵ that the reaction of neopentyl iodide with concentrated alcoholic potassium hydroxide gives but 12-13 % of the product expected from bimolecular nucleophilic substitution (neopentyl ethyl ether), the major product consisting of neopentane. The figure recorded here represents the total rate of removal of the halogen, and, until the reaction products have been analysed under our experimental conditions, it must be regarded as an upper limit for the rate of reaction (S_N2).

TABLE VIII.

RELATIVE RATES OF SUBSTITUTION OF PRIMARY ALKYL BROMIDES.

Bromide.		Methyl.	Ethyl.	n-Propyl.	isoButyl.	Neopentyl.
Approx. Relative Rates (Et = 1)	Bimolecular reaction (a) *	$\sim 12^\ddagger$	I	0.28 ‡	0.029 ‡	6.5×10^{-6}
	Solvolytic reaction (b) ³³ *	1.8	I	0.54	0.075	0.0052
	" Silver-ion " reaction (c) ³³ †	0.81	I	0.60	0.084	0.013

* Relative rates at 95°.

† Relative rates at 64°.

‡ Calculated by assuming an activation energy of 21 Cals. (the value found for EtBr; ³⁴ cf. Table VII); the activation energies of all the principal reactions are being determined.

hydrogen atoms are replaced,³⁶ because this influence should operate more strongly in unimolecular solvolytic reactions, and this is contrary to the facts, as we shall show when we consider such reactions. There are further reasons. The electromeric factor should produce a more steady logarithmic decrease in the rate from ethyl to neopentyl, and is not competent to interpret the much enlarged gap between *isobutyl* and neopentyl. Again the loss of β -hydrogen is just as complete in

³² Hughes, Ingold, Masterman and MacNulty, *J.C.S.*, 1940, 899.

³³ Unpublished experiments by I. Dostrovsky.

³⁴ Grant and Hinshelwood, *J.C.S.*, 1933, 258.

³⁵ Whitmore, Wittle and Popkin (*loc. cit.*, p. 621).

³⁶ This is the effect brought to light by Baker and Nathan (*J.C.S.*, 1935, 1844).

methyl as in neopentyl, but the differences between each of these and ethyl are qualitatively opposite. It is therefore concluded that in addition to the retarding influence of methyl substitution, which operates throughout the series, and may be attributed essentially to the inductive effect, there is a superposed effect, which may in principle enter in all stages of β -substitution, but which assumes real importance only in the case of the neopentyl halide.

This effect is believed to be of steric origin. It is generally agreed that the most favourable configuration for the transition state of a bimolecular substitution is that in which the entering and leaving groups and the α -carbon atom lie on or near a straight line, the other attached groups being on or near a plane perpendicular to that line. Assuming for simplicity that the groups lie on an exact straight line and a perpendicular plane, the β -methyl radical of the *n*-propyl group could lie in this plane; but the two β -methyl radicals of the *iso*-butyl group would be most favourably situated in other planes through the $C_\alpha-C_\beta$ bond inclined at 30° to the first plane; and two of the three β -methyl substituents of the neopentyl group would be found in planes inclined at 60° to the original plane. Thus, as a short calculation shows, the clearance* between the β -methyl substituents and the attacking and displaced atoms decreases by about 0.5 Å. for each additional β -methyl radical. No doubt this rapid contraction is lessened by some departure of the reacting configuration from a strictly linear one. Nevertheless, even in the *n*-propyl case the clearance, about 3.3 Å. or a little more depending on the departure of the reacting configuration from linearity, is of about the magnitude for which some steric effect due to repulsion energy would begin to show if only a slight contraction were made. What seems certain is that an effect of this kind must enter if any contraction approaching 1 Å. is made. Furthermore we may be sure that such an effect would become prominent suddenly, owing to the rapid steepening which all repulsive energy curves exhibit when the distance is decreased beyond a certain more or less critical amount. From this point of view the factor of 2×10^{-4} between the rates for *isobutyl* and neopentyl bromides seems quite reasonable.

The rate variation among the members of the alkyl series is similar in type in the solvolytic reactions (*b*), except that the differences between the rates are reduced, and the last difference so much reduced that neopentyl bromide although the slowest of the halides by a considerable margin is to nothing like the same extent in a peculiar position. These solvolytic reactions are all of the first order (solvent in excess). We have, however, observed a very powerful effect of added alkali in the case of the first four members; there is little doubt, therefore, that the reactions of these four halides are predominantly bimolecular (S_N2), the solvent molecules functioning as nucleophilic reagents. The rate variation is of a type which can be attributed to the inductive effect.

In the solvolytic reaction of neopentyl bromide, however, the bimolecular mechanism is inhibited so effectively that the reaction in

* By "clearance" is meant the maximum (and therefore the effective) value, that can be produced by rotation around single bonds, of the distance between the attacking or displaced atom and whichever methyl substituent is nearest. The distances are reckoned between atomic nuclei, and for purposes of calculation the methyl group is treated as a pseudo-atom whose nucleus is the carbon nucleus.

aqueous alcohol shows no alkaline catalysis, the rate being the same in acid, neutral or alkaline solution. This is a familiar criterion of mechanism, here reinforced by the remarkable unresponsiveness of the halide to bimolecular attack even by the very strongest bases. It is concluded that the mechanism of the hydrolysis of neopentyl bromide in aqueous alcoholic solution is unimolecular. Thus the rate, instead of dropping practically to zero from *isobutyl* to neopentyl, drops only to about one-fifteenth, this residual value representing the unimolecular rate for neopentyl bromide, and the order of magnitude of the (usually unobservable) unimolecular rates for primary halides generally.

It should be emphasised that this unimolecular rate is observed in a highly aqueous solvent (equal volumes of ethyl alcohol and water) and that it would be incomparably smaller in dry ethyl alcohol, the solvent used for the study of the alkaline reactions. The rate of bimolecular reaction with an anion, on the other hand, is reduced on passing from the dry alcoholic to the aqueous solvent.

We cannot, of course, compare the unimolecular rates for the primary bromides, but they are expected to increase from methyl to neopentyl. We can, however, compare the unimolecular rates for neopentyl and *tert.*-butyl bromides,^{9, 37} and we find that the latter rate is about 10^8 times larger. It is already known that the unimolecular rate for *tert.*-butyl bromide is about 10^4 times larger than for *isopropyl* and other secondary alkyl bromides.^{10, 37}

We may briefly consider an alternative explanation of the variation of rate in the solvolytic reactions, namely, that the electrons forming the β -C—H bonds participate in an electromeric displacement which diminishes as the hydrogen atoms are replaced (*cf.* above). This effect is obviously of the correct type for an explanation of the decrease in rate from ethyl to neopentyl, and the difficulty which it introduces regarding the high reactivity of the methyl group could be minimised by drawing attention to the possible influence of the size of the group in determining the solvation of the transition state.³⁸ This explanation should, however, apply most effectively to the ionisation mechanism, and we can show that when ionisation is most certainly in operation (*e.g.*, in the tertiary alkyl halides) it completely fails to represent the facts. The differences in the rates of solvolysis (in aqueous alcohol) of the secondary alkyl halides, *e.g.*, Me_2CHBr , EtCHMeBr , Et_2CHBr , are small and irregular,³⁹ but in the tertiary series the replace-

TABLE IX.
UNIMOLECULAR RATE CONSTANTS FOR THE HYDROLYSIS OF TERTIARY
ALKYL HALIDES.

Chloride.	No. of β -H Atoms.	$10^6 k_1 (\text{sec.}^{-1})$.
$\text{CH}_3 \cdot \text{CMe}_2\text{Cl}$ (<i>tert.</i> -butyl)	9	0.854 ⁴⁰
$\text{CH}_3\text{CH}_2 \cdot \text{CMe}_2\text{Cl}$ (<i>tert.</i> -amyl).	8	1.50 ⁴¹
$(\text{CH}_3)_3\text{C} \cdot \text{CEt}_2\text{Cl}$ (α , α -diethylnopentyl).	4	11.7 ⁴²

³⁷ Cooper and Hughes, *J.C.S.*, 1937, 1183.

³⁸ *Cf.* Baughan, Evans and Polanyi, *Trans. Faraday Soc.*, 1941, 37, 377.

³⁹ Unpublished experiments by M. L. Dhar.

⁴⁰ *Cf.* Cooper, Hughes and Ingold, *J.C.S.*, 1937, 1280.

⁴¹ Hughes and MacNulty, *ibid.*, 1283.

⁴² Bartlett and Knox, *J. Amer. Chem. Soc.*, 1939, 61, 3184.

ment of the β -hydrogen atoms by alkyl groups results in a substantial increase of rate. The results for the hydrolysis of three tertiary halides (one of which contains a neopentyl system) are listed in Table IX, where k_1 represents the rate of ionisation ($k_{S_N1} + k_{EI}$)⁴⁰ in "80 %" aqueous ethyl alcohol at 25°.

This does not mean that the electromeric effect does not exist, but only that the inductive effect is stronger in these examples. So far, it is only in cases in which the electromeric effect is magnified by the extra resonance energy arising from the insertion of $p\text{-C}_6\text{H}_4$ between the operative CH -bonds and the seat of reaction that we have found the electromeric effect to dominate.⁴³

As already stated the "silver-ion" reaction is not suitable for accurate rate comparisons. We note, however (*cf.* Table VIII), that the differences between the bimolecular and the solvolytic reactions are now emphasised, *i.e.*, the effect of β -alkyl substitution is further reduced, and the rate for methyl bromide is now reduced below that for ethyl bromide. The results are consistent with the hypothesis that the effects which are expected to be associated with the unimolecular mechanism are now making a more appreciable contribution to the variation of rate in the series as a whole. We hope to improve on this demonstration by working with suitable electrophilic catalysts in homogeneous solution.

(2) Polyhalogen Compounds.

As a second example of the application of the principles outlined in Part I, we shall briefly consider the question of the reactivity of the polyhalogen compounds in hydrolysis. The discussion will be mainly confined to the dihalogen compounds (the application to more complex structures being, in principle, the same), and our thesis will be that the effect of a second halogen is intimately dependent on mechanism.

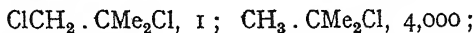
Two principal cases arise depending on whether the two halogen atoms are attached to the same or to different carbon atoms. In the former circumstance, an electron-release process, $\text{Cl}-\text{C}(\text{Cl})$, will inhibit the approach of the nucleophilic reagent necessary for mechanism S_N2 , and facilitate the rate-determining ionisation of mechanism S_N1 . Thus it is found that in a structure predisposed to react by mechanism S_N2 (*e.g.*, CH_3Cl) the introduction of a second halogen atom (*e.g.*, in CH_2Cl_2) has an inhibitory effect on the hydrolysis. On the other hand, when a monohalide, owing to the presence of a strongly electron releasing group, such as phenyl, has already a moderately developed tendency to react by mechanism S_N1 (*e.g.*, benzyl chloride), then the introduction of additional α -chlorine atoms (as in benzal chloride and benzotrichloride) produces a greatly enhanced reactivity, the operative mechanism now being S_N1 .⁴⁴

When the second halogen atom is in a position other than the seat of reaction, the above electron-release mechanism is unavailable. In this event, the ordinary electron-attracting effect controls the situation, and this facilitates mechanism S_N2 and retards S_N1 . Examples of the facilitating influence of a β -halogen substituent in bimolecular reactions have been previously noted.⁴⁵ The inhibitory effect on the unimolecular mechanism may be illustrated by the comparative first-order rates re-

⁴³ Hughes, Ingold and Taher, *J.C.S.*, 1940, 949.

⁴⁴ Olivier and Weber, *Rec. trav. chim.*, 1934, 53, 869.

corded for the reactions of *tert.*-butyl chloride and 1, 2-dichloro-2-methylpropane in 80 % aqueous ethyl alcohol.^{9, 45} (Relative rates :



the halogen attached to the tertiary carbon atom is eliminated in both examples.)

(3) Effects due to Carbonyl Group.

The carbonyl group figures prominently in the reactions of $\text{O}=\text{C}-\text{X}$ such as the hydrolysis or alcoholysis of acid chlorides ($\text{X} = \text{Cl}$), anhydrides ($\text{X} = \text{O}-\text{C}=\text{O}$), amides ($\text{X} = \text{NH}_2$), acids ($\text{X} = \text{OH}$) and

esters ($\text{X} = \text{OR}$). The effect of the polarisation, $\overset{\curvearrowright}{\text{O}}=\text{C}-\text{X}$, which this group manifests in most of its reactions will facilitate mechanism $\text{S}_{\text{N}}2$ and inhibit mechanism $\text{S}_{\text{N}}1$, and this is borne out by the powerful effect of hydroxide and alkoxide ions which is usually observed in these reactions. It is, of course, well known that water or alcohol alone can effect many of these substitutions, and catalysis by acids is very commonly observed. Concerning the action of the nucleophilic reagent, it has been shown⁴⁶ that the etholysis of benzoyl and *p*-nitrobenzoyl chlorides in acetone-ethyl alcohol solvents is subject to very powerful catalysis by ethoxide ions, and the magnitude of the effect in this bimolecular reaction with the anions makes it probable that the reaction with the solvent is also bimolecular ($\text{S}_{\text{N}}2$) (*cf.* p. 612). The accumulation of electron-releasing substituents in the phenyl nucleus, however, promotes the unimolecular mechanism ($\text{S}_{\text{N}}1$), and our results indicate that this mechanism is of considerable importance in the case of 2 : 4 : 6-trimethylbenzoyl chloride, which shows but a small alkaline catalysis.

It is sometimes found that both electron-releasing and electron-attracting groups (*e.g.*, CH_3 and NO_2) exert a facilitating influence on the solvolytic reactions of substituted benzoyl chlorides.^{46, 47, 48} This could be simply explained in terms of a change of mechanism. The same idea may be useful in explaining some of the effects of changing the position of the substituent in the nucleus.⁴⁸ The methyl and nitro-groups form an interesting contrast in this respect. When both accelerate, the methyl is most effective, and the nitro-group least effective, in the ortho-position. The interpretation would be that the methyl group facilitates mechanism $\text{S}_{\text{N}}1$, whilst the nitro-group accelerates mechanism $\text{S}_{\text{N}}2$. But bimolecular reactions, in the transition states of which five groups are partly or wholly covalently attached to a single carbon atom, are subject to steric hindrance arising from the repulsive forces between the groups (*cf.* Part II, Section 1). On the other hand, unimolecular reactions never involve the attachment of more than four groups to any carbon atom, the additional forces entering in the transition state of the rate-determining step being of the longer-range electrostatic type; accordingly steric hindrance is rare in these reactions

⁴⁵ Brown, Kharasch and Chao, *J. Amer. Chem. Soc.*, 1940, **62**, 3435.

⁴⁶ Unpublished experiments by E. R. A. Peeling.

⁴⁷ Berger and Olivier, *Rec. trav. chim.*, 1927, **46**, 516, 861.

⁴⁸ Norris and Ware, *J. Amer. Chem. Soc.*, 1939, **61**, 1418.

(*cf. loc. cit.*, p. 621; also the paper by Day and Ingold, *this vol.*, p. 686). Allowing for this difference we find the observations entirely intelligible.

Concerning acid catalysis, we reflect that hydrogen ions might *a priori* participate in the reaction by co-ordination either with the carbonyl group (*e.g.*, $\text{HO}=\overset{+}{\text{C}}-\text{X}$) or with the group to be expelled,

if the latter is sufficiently basic (*e.g.* $\text{O}=\text{C}-\overset{+}{\text{OHR}}$ and $\text{O}=\text{C}-\overset{+}{\text{NHR}}_2$).

The former effect would favour reaction by mechanism $\text{S}_{\text{N}}2$, and the latter should facilitate reaction by both mechanisms. The demonstrated absence of acid catalysis in the hydrolysis of benzoyl chloride^{46, 47} would seem to show that the proton uptake occurs at the basic replaceable groups, and that co-ordination with the carbonyl group is of negligible importance in the case of the acid halides, if not in general.

When a carbonyl group is attached to the centre of substitution, as in the α -halogeno-ketones, the usual carbonyl polarisation,

$\text{O}=\text{C} \leftarrow \text{C}-\text{Cl}$, should again favour the bimolecular mechanism. These halides are in fact extremely reactive in bimolecular substitution; chloroacetone for instance reacts with iodide ions in acetone about 35,000 times more easily than *n*-propyl chloride.⁴⁸ These reactions are known to be bimolecular.

(4) Effects due to Vinyl and Aryl Groups.

A double bond at the seat of substitution, as in the vinyl and phenyl halides, induces an electromeric displacement, $\text{C}=\text{C} \leftarrow \text{Hal}$, which, since it opposes the activation, $\text{C}-\text{Hal}$, must strongly inhibit mechanism $\text{S}_{\text{N}}1$ and also retard mechanism $\text{S}_{\text{N}}2$, although to a smaller extent. It is to be anticipated therefore that substitution in these systems never occurs by mechanism $\text{S}_{\text{N}}1$ and only with difficulty by mechanism $\text{S}_{\text{N}}2$; and this is borne out by general experience. There is an apparent difficulty, however, when we consider the case of the polynitro-aromatic halides such as picryl chloride. The effect of the electron-attracting nitro-groups should greatly facilitate mechanism $\text{S}_{\text{N}}2$ and should further retard mechanism $\text{S}_{\text{N}}1$; but it is well known that these halides suffer rapid hydrolysis or alcoholysis in aqueous or alcoholic solution in the absence of any powerful nucleophilic reagents. A kinetic study of the effect on the reaction rate of adding more powerful nucleophilic reagents (*cf.* p. 612) has, however, made it most probable that the solvent molecules are themselves functioning as nucleophilic reagents.⁵⁰ The bimolecular mechanism has evidently been favoured to such an extent that even these weakly basic reagents are now able to participate in a facile displacement of halogen in an aromatic halide.

(5) Effects due to Allyl Groups.

When the unsaturation is one carbon atom removed from the centre of substitution, as in the benzyl and allyl halides, the situation is quite different from that depicted in the preceding section. In this system

⁴⁸ Conant, Kirner and Hussey, *J. Amer. Chem. Soc.*, 1925, 47, 488.

⁵⁰ Unpublished experiments by J. Graham.

the electromeric polarisation, $\text{C}=\text{C}^{\leftarrow}\text{C}^{\rightarrow}\text{Hal}$, may be expected to have a very strong facilitating influence on mechanism $\text{S}_{\text{N}}\text{I}$, and a similar, though less powerful, effect on mechanism $\text{S}_{\text{N}}2$; while the alternative

polarisation, $\text{C}^{\leftarrow}=\text{C}-\text{C}^{\rightarrow}\text{Hal}$, could also be effective in facilitating the bimolecular mechanism.* Such halides may therefore be expected to be highly reactive under all conditions of nucleophilic substitution, and there is published evidence that this is actually the case.⁴

A comparison of the rates of hydrolysis and alcoholysis of a number of allyl halides, with the corresponding rates for the related saturated compounds, has revealed many interesting points which confirm the theory in some detail.⁵¹ For convenience in reference the various chlorides examined are distinguished numerically, as indicated in the scheme below:

<i>Unsaturated Chloride.</i>	<i>Saturated Chloride.</i>	
(ia) $\text{CH}_2=\text{CH} \cdot \text{CH}_2 \cdot \text{Cl}$ (Allyl)	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Cl}$ (ib)	(<i>n</i> -propyl)
(iia) $\text{CH}_2=\text{CH} \cdot \text{CHMe} \cdot \text{Cl}$ (α -methylallyl)	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{Cl}$ (iib)	(<i>sec.</i> -butyl)
(iiia) $\text{CH}_2=\text{CMe} \cdot \text{CH}_2 \cdot \text{Cl}$ (β -methylallyl)	$\text{CH}_3 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{Cl}$ (iiib)	(<i>iso</i> -butyl)
(iva) $\text{Me} \cdot \text{CH}=\text{CH} \cdot \text{CH}_2 \cdot \text{Cl}$ (γ -methylallyl)	$\text{Me} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Cl}$ (ivb)	(<i>n</i> -butyl)
(va) $\text{Ph} \cdot \text{CH}=\text{CH} \cdot \text{CH}_2 \cdot \text{Cl}$ (γ -phenylallyl)	$\text{Ph} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Cl}$ (vb)	(γ -phenyl- <i>n</i> -propyl)

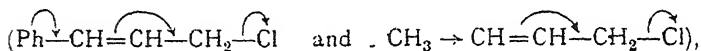
The reactions examined kinetically were those with (1) sodium ethoxide in dry ethyl alcohol, and (2) aqueous ethyl alcohol (mainly "50 %") in initially neutral solution. Under the former conditions all the reactions are of the second order and evidently bimolecular; under the latter conditions all are first order, but some are bimolecular while others are unimolecular (*cf.* below). The second-order (bimolecular) rate constants for the unsaturated halides are greater than for the related saturated halides by factors of the order $10\text{--}10^2$, while the first order constants of the former are greater than the corresponding constants of the latter by widely varying factors of the order $10\text{--}10^2$ (i and iii), 10^3 (ii and iv) or 10^4 (v).

The widely different factors for the solvolytic reactions may be explained as follows. The rates of hydrolysis of the allyl and β -methylallyl halides (ia and iiia) are markedly increased by alkali, and it is probable that, even in neutral or acidic solutions, the reactions of these compounds are partly or wholly bimolecular, the solvent molecules functioning as nucleophilic reagents. Since the same is undoubtedly true of the related saturated halides (ib and iiib) with which comparison is made, it follows that the lowest factors ($\sim 10\text{--}10^2$) relate substantially to the bimolecular mechanism ($\text{S}_{\text{N}}2$), and it is significant that these figures are of the same order of magnitude as those observed for the

* The electrical requirements of the associative (bond-forming) and dissociative (bond-breaking) processes in bimolecular substitution are qualitatively opposite, and it is not always possible to forecast what the net requirements will be. In this instance the attached system can respond to demands of either sign.

⁵¹ Unpublished experiments by A. G. Catchpole.

bimolecular reactions with ethoxide ions. On the other hand, the first-order reactions of α -methylallyl and γ -phenylallyl chlorides (iia and va) are unaffected by dilute alkali, and the rate for γ -methylallyl chloride (iva) is only slightly increased; these reactions are therefore substantially unimolecular (*cf.* p. 612). This is also true of the saturated halide (iib) with which the α -methyl derivative is compared, so that the rate factor ($\sim 10^3$) in this instance refers to the effect of unsaturation on the unimolecular mechanism. The hydrolysis of the saturated analogues (ivb and vb) of γ -methylallyl and γ -phenylallyl chlorides (iva and va), like that of most primary halides, is bimolecular, so that any concomitant (unobserved) unimolecular reaction must be slower; therefore if unimolecular rates could be compared throughout, the effects of unsaturation in these examples would be even larger than those actually observed (factors $\sim 10^3$ and 10^4). The unsaturation factor is enhanced in the γ -methylallyl and γ -phenylallyl halides (iva and va) because the effects of the methyl and phenyl groups (which are always large in the unimolecular mechanism) are transmitted with undiminished power to the seat of substitution

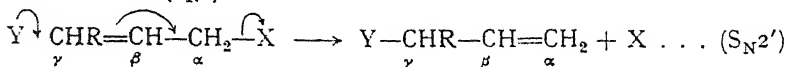


whereas they are greatly reduced in the corresponding saturated halides (ivb and vb) by relay through the intervening saturated carbon atoms.

The rates (at 40°) for the solvolytic reactions of the unsaturated chlorides are in the order: γ -phenylallyl $\gg \gamma$ -methylallyl $\sim \alpha$ -methylallyl $\gg \beta$ -methylallyl \sim allyl; while the rates (at 100°) for the bimolecular reactions with sodium ethoxide follow the sequence: γ -phenylallyl $> \gamma$ -methylallyl $>$ allyl $> \beta$ -methylallyl $> \alpha$ -methylallyl.* The sequence for the unimolecular solvolytic reactions is unequivocally predicted by theory, while the sequence for the bimolecular reactions, though not unequivocally predicted owing to the ambiguous electrical needs of the bimolecular mechanism, is quite consistent with the theoretical principles already illustrated.

(6) Application to Anionotropy.

In a previous discussion of this problem,¹ it was stated that, in addition to the usual unimolecular and bimolecular mechanisms (S_N1 and S_N2),[†] there is a third possible process by which a nucleophilic substitution may be effected in allylic compounds, *viz.*, a bimolecular mechanism involving attack by the nucleophilic reagent at C_γ (S_{N2}'), and not at C_α (S_{N2}):



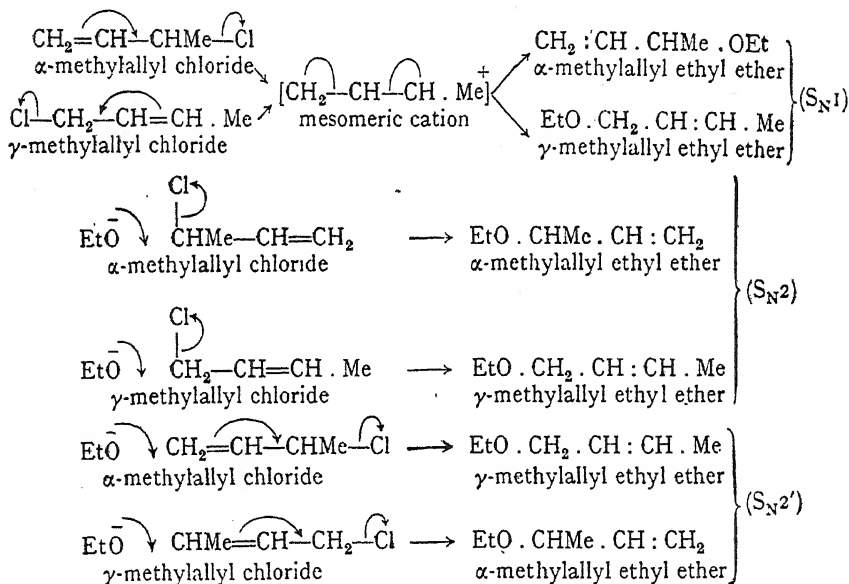
* The relative reactivities of allyl chloride, β - and γ -methylallyl chlorides, and 1-chloro-2-methyl-2-butene, in their reactions with sodium ethoxide in dry ethyl alcohol (at 35° and 50°), have been recorded by Tamele, Ott, Marple and Hearne in a recent paper (*Ind. Eng. Chem.*, 1941, 33, 115) dealing mainly with the reactions of β -methylallyl chloride. In so far as comparison can be made, their results and ours are in substantial agreement.

† The application, to the problem of anionotropy, of the theory envisaging two mechanisms of substitution (S_N1 and S_N2) has also been made by Arcus and Kenyon (*J.C.S.*, 1938, 1912), and similar mechanisms have been discussed in this connection by Young and Lane (*J. Amer. Chem. Soc.*, 1938, 60, 847; *cf.* Young and Nozaki, *ibid.*, 1940, 62, 311).

The unimolecular and the bimolecular mechanisms can usually be distinguished kinetically, and the observations summarised in the last section indicate that both mechanisms may operate under favourable circumstances. In order to distinguish between the two possible bimolecular mechanisms, and to obtain further information regarding the problem as a whole, it is, however, necessary to undertake a parallel study of both the kinetics and the products of reaction in an appropriate system.

This has been carried through for the reactions of α - and γ -methylallyl chlorides, (a) with sodium ethoxide in ethyl alcohol, and (b) with ethyl alcohol in the absence of any extraneous reagent.⁵¹ The bimolecular reaction with sodium ethoxide results in the exclusive production of the ethyl ether corresponding to the halide undergoing reaction. The solvolysis reaction with ethyl alcohol, on the other hand, gives rise to a mixture of the two possible ethyl ethers, and the composition of the mixture is the same no matter which halide is used initially.*

The following scheme shows the products to be expected from the operation of the three mechanisms under consideration; what the observations show is that, whilst mechanisms S_N1 and S_N2 give the products indicated, mechanism S_N2' is not apparent:—



It should be emphasised that the possibility of reaction by mechanism S_N2' cannot in general be excluded on the basis of so limited a series of observations as that described above. If this be admitted, it follows that intervention by extraneous anions in anionotropic change does not, contrary to a common assumption, rigidly demonstrate the intermediate formation of a carbonium ion.⁵²

* The results recall the observations of Meisenheimer and Beutter (*Annalen*, 1934, 508, 58), who obtained only cinnamyl acetate from cinnamyl chloride and sodium acetate in acetic anhydride, and a mixture of cinnamyl and α -phenylallyl acetates from cinnamyl chloride and acetic acid.

⁵² Cf. Burton, *J.C.S.*, 1934, 1268.

A summary of the principles outlined in Part I to the problem of the Walden inversion would be too long for inclusion here, and a later opportunity must be taken to bring up to date the summaries already available.^{2, 53}

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Aberystwyth.*

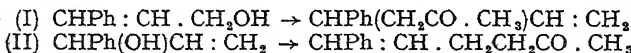
⁵³ Cowdrey, Hughes, Ingold, Masterman and Scott, *ibid.*, 1937, 1252; *cf.* also, Bateman, Church, Hughes, Ingold and Taher, *ibid.*, 1940, 1010.

GENERAL DISCUSSION

Prof. F. G. Donnan (*London*): I should like to ask Ingold when the rate of ionisation of organic compounds was first considered as a speed-controlling step in the kinetic analysis of "organic" reactions in liquid systems. It is of the greatest interest that considerations of this type play a notable rôle in the fundamental investigations of Ingold and Hughes. I think that a historical note on this matter would be welcomed by all progressive chemists.

Prof. C. K. Ingold (*London-Aberystwyth*), in reply said: The idea of ionisation as a rate-controlling process in organic reactions was in the minds of several German organic chemists towards the end of the last century. It was expressed by Knorr¹ and particularly clearly by Wislicenus² in relation to prototropic change.

Dr. C. L. Wilson (*Manchester*) said: Although clear evidence for a bimolecular substitution with rearrangement (S_N2') in an anionotropic system has not so far been produced, there are indications that such a reaction has already been carried out, but its mechanism not appreciated, by Carroll.³ This author reacted compounds such as acetoacetic ester with $\beta\gamma$ -unsaturated alcohols under alkaline conditions, and there is reason to believe (the argument will be published elsewhere) that the important stage in the process is a reaction between an ester (acetate or aceto-acetate) of the alcohol and the anion (by proton removal) of acetoacetic ester. With cinnamyl alcohol (I) and its isomer (II), Carroll was able to isolate by reaction with acetoacetic ester only the rearranged product (a ketone) in each case.



Since unimolecular ionisation operating in both cases would be expected to give the same product, or mixture of products, one or both series of reactions would seem to involve substitution (presumably bimolecular) with rearrangement.

Could Hughes help in the choice of the best experimental conditions for the alkylation of bases using halides? For example, with aniline and isopropyl bromide in a hydroxylic solvent the products are isopropyl aniline, propylene and products of solvolysis. The use of a nonreactive solvent would certainly help, but can one favour alkylation at the expense of elimination? Whilst isopropyl bromide is, perhaps, a rather difficult example to discuss owing to possible duality of mechanism, would not the use of low temperatures, a solvent of high dielectric constant (to favour unimolecular processes), and a medium of low basicity be the right kind of choice?

¹ Knorr, *Annalen*, 1896, 293, 38.

² Wislicenus, *Über Tautomerie*, Stuttgart, 1898, p. 187.

Dr. E. D. Hughes (*London-Aberystwyth*), in reply to Wilson, said: On theoretical grounds a bimolecular substitution with rearrangement in anionotropic systems (Mechanism S_N2') seems a very natural event, and it is interesting to find experimental indications of its existence. The reactions described by Carroll (cited by Wilson) may include a substitution of this type, but further evidence of mechanism (particularly kinetic evidence) is desirable.

The factors determining the relative ease of substitution and elimination in the reactions of organic bases with alkyl halides have not been fully investigated, but the alkylation would probably be favoured by the conditions mentioned by Wilson and by the use of alkyl chlorides (rather than bromides or iodides). Under the most favourable conditions, the method is unsatisfactory for secondary alkyl halides and practically useless for the tertiary compounds.

³ *J. Chem. Soc.*, 1940, 704, 1266; 1941, 507.

MECHANISM AND KINETICS OF AROMATIC SIDE-CHAIN SUBSTITUTION. INTERPRETATION OF REACTION DATA BY THE METHOD OF RELATIVE ENERGY LEVELS.

By JOHN WILLIAM BAKER.

Received 21st August, 1941.

Classification of Side-chain Substitution Reactions.

With the development of modern electronic theories of organic reactions the study of aromatic side-chain substitution became an attractive and fertile field for research. Two features contributed towards this popularity. Firstly, the nature of the aromatic electronic system permits the ready transmission of electron-flow either towards or away from the seat of reaction in the side-chain: hence, with nuclear substitution by groups of known polar character, the relative increase or decrease in electron-density at the reaction centre could be assessed, at least qualitatively, particularly in view of the large amount of data available concerning the effect of the same substituents on aromatic nuclear substitution. Secondly, such substitution (except in the *ortho*-position) occurs at a point sufficiently distant from the reacting group to eliminate any serious disturbance due to purely spatial effects; hence the observed effects on reaction velocity could, with a reasonable degree of certainty, be ascribed to the resultant alteration in electron-availability in the side-chain. This information, coupled with that obtained by the more usual methods of kinetic analysis, provides a basis for the elucidation of mechanism and, conversely, once the intimate mechanism has been established, the reaction may be used to examine the polar character of other substituent groups.

The classification of side-chain reactions put forward by Ingold and Rothstein¹ was formulated on this basis and recognised two main types, each of which was capable of sub-division into two sections according to the nature of the mechanism of substitution.

¹ *J.C.S.*, 1928, 1217.

Type A.—Side-chain reactions which require electron-accession from the aromatic nucleus towards the side-chain, such increased electron-density being required (1) for the liberation of an anion, or (2) for the electrostriction of a cation.

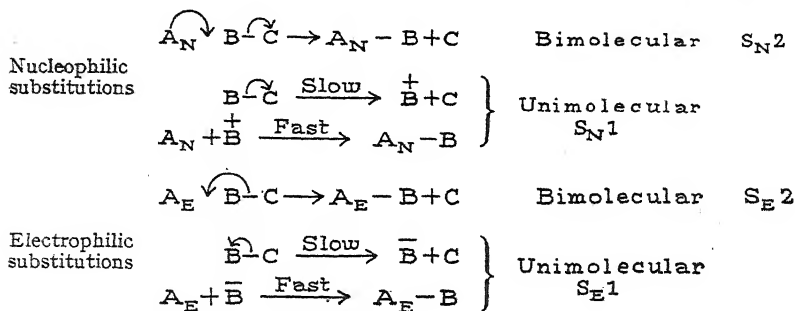
Type B.—Side-chain reactions requiring electron-recession from the side-chain to the aromatic nucleus, the resulting decreased electron-density effecting (1) the liberation of a cation, or (2) the electrostriction of an anion.

One important criterion in assigning a reaction to one or other of these classes was the effect of substituents on the reaction velocity, since type A reactions should be accelerated by the introduction of electron-release groups into the aromatic nucleus and retarded by substitution of electron-attracting groups. Type B reactions, conversely, would be retarded by the former and accelerated by the latter type of substituent. The great increase in our knowledge of the mechanisms of substitution reactions which has occurred as a result of recent extensive investigations, notably by Ingold, Hughes and their collaborators, has made it clear that the application of this criterion is not as simple as superficial examination might suggest, but it still remains a most useful method of attack on the mechanisms of side-chain reactions, and is one with which this review is chiefly concerned. Attention will be directed almost exclusively towards bimolecular, nucleophilic substitutions, since these, as is shown below, constitute the more complex problem.

The recent work on substitution at saturated carbon and the theoretical views to which it has led have been adequately summarised in a recent discussion by Hughes,² and have been extended and confirmed in a later series of papers by Ingold *et al.*³ Briefly the essential points are as follows:—

(1) Attacking reagents are classified into two types: (a) nucleophilic, *i.e.* those which have a constitutional affinity for positive centres and which, in reaction, transfer electrons to or share their electrons with a foreign nucleus, and (b) electrophilic reagents which have an affinity for negative centres and which thus acquire electrons or a share in electrons belonging to some other atom or ion.

(2) The kinetic differentiation of reactions into (a) unimolecular* and (b) bimolecular mechanisms which, for a reaction of the type $A + BC \rightarrow AB + C$, may be represented by the the general schemes:—



² *Trans. Faraday Soc.*, 1938, 34, 185.

³ *J.C.S.*, 1940, 899, *et. seq.*

* *Cf.* Bateman, Church, Hughes, Ingold and Taher, *ibid.*, 1908, for a note on nomenclature.

where A_N and A_E represent a nucleophilic and electrophilic reagent respectively. It should be noticed that Ingold and Rothsteins' two main reaction types A and B cannot be correlated, respectively, with electrophilic and nucleophilic substitutions: thus although, for example, the rate-determining ionisation in the S_N1 mechanism would be greatly facilitated by electron-release towards the side-chain, the whole reaction is a nucleophilic substitution. A similar, but converse, argument obviously applies to the S_E1 mechanism.

Bimolecular Nucleophilic Substitution.

In the case of bimolecular mechanisms the position is more complicated: thus in the S_N2 mechanism the energy requirements of the breaking of the bond B—C (included in the term "chemical inertia" by Evans and Polanyi⁴), and of the formation of the bond A—B ("chemical driving force") cannot be separated, but the former process should be facilitated by electron-accession, whereas the approach of the nucleophilic reagent A_N to form the bond A—B should be favoured by electron-recession. It is because of these dual, conflicting polar requirements that the effect of substituents on the velocity of a bimolecular substitution is always smaller in magnitude, and less clear-cut in nature, than in the case of a unimolecular substitution with its unambiguous requisites in electron displacements.⁵ A striking example of this is the clear-cut demonstration of the tautomeric effect of alkyl groups in the unimolecular solvolysis of *p*-alkylbenzhydryl halides⁶ contrasted with the much less definite indication in the bimolecular nucleophilic reaction of *p*-alkylbenzyl halides with pyridine, on which Baker and Nathan⁷ based their original theory of the conjugation of alkyl groups with attached, unsaturated systems. Further reference to this point is made later (p. 639).

The development of the modern theory of a displacement reaction due to London⁸ and Polanyi,⁴ which postulates that the reaction $A + BC \rightarrow AB + C$ proceeds through the transition complex $A \cdots B \cdots C$, has, however, provided a physical basis for the assessment of the effect of substituents on a bimolecular reaction. It has been pointed out by Hughes, Ingold, Masterman and McNulty⁹ that the alterations in electron-density which arise from the introduction of a substituent are to be correlated with changes in the energy levels in the molecule. Anything analogous to conjugation lowers the energy level and stabilises the system. It is thus possible to assess, at least qualitatively, the effects of substituents of known polar character by considering their relative stabilising effects (due to increased resonance) on the initial, transition and final states of the reacting system, and thus on the energy of activation of the reaction or on the position of an equilibrium. Since it is generally accepted (as electronic theory requires) that, with substituents sufficiently removed from the centre of reaction, their effects on reaction velocity arise mainly from their effect on the energy of activation, determination of such reaction velocities provides a means of confirming a theoretically probable mechanism of reaction.

⁴ *Trans. Faraday Soc.*, 1938, 34, 11.

⁵ Cf. Baker, *J.C.S.*, 1933, 1128; Hughes, Ingold and Taher, *ibid.*, 1940, 949.

⁶ Hughes, Ingold and Taher, *loc. cit.*

⁷ *J.C.S.*, 1935, 844.

⁸ *Z. Elektrochem.*, 1929, 35, 552.

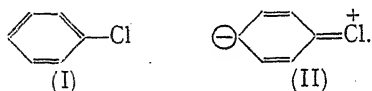
⁹ *J.C.S.*, 1940, 899.

It thus becomes important to consider the canonical structures in the resonance hybrid of the ground state of any molecule to be involved in reaction, since these may be assumed to influence the types of electron displacement by which reaction is most probable, *i.e.* the mechanism by which a molecule is "predisposed" to react.¹⁰ The application of this method of approach may be suitably exemplified by the attack of nucleophilic reagents of the type NR_3 , ROH , etc., on the series of derivatives of types ArX , ArCH_2X , $\text{ArCH}_2\text{CH}_2\text{X}$, $\text{ArCO}\cdot\text{X}$ and $\text{ArCO}\cdot\text{CH}_2\text{X}$ (X = halogen).

Nucleophilic Attack.

(1) On Halogenobenzenes.

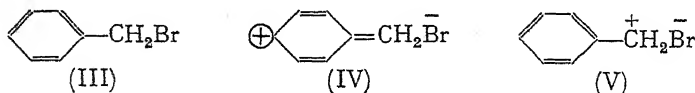
A monohalogenobenzene such as chlorobenzene is represented in the ground state of the molecule as a resonance hybrid of structures of types (I) and (II), since the $\text{C}-\text{Cl}$ bond distance is $0.06-0.07 \text{ \AA}$ less than



the normal value in a saturated chlorohydrocarbon, representing *ca* 15 % of double-bond character.¹¹ The incursion of dipolar structures of type (II) will greatly reduce any tendency for chlorine to separate as an anion, whilst the increased electron density in the benzene ring is prejudicial to the electrostriction of a nucleophilic reagent. The inertness of such compounds towards nucleophilic reagents (OH^- , NH_2^- etc.) unless the nuclear polarisation is reversed by suitable attachment of strongly electron-attracting groups such as nitro, is axiomatic.

(2) On Benzyl Halides.

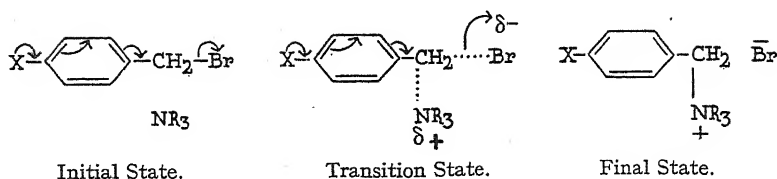
(a) **Attack by a neutral molecule.**—In the benzyl halides the intercalation of a saturated methylene group between the halogen atom and the aromatic nucleus precludes the type of conjugation present in the halogenobenzenes, and molecules such as benzyl bromide will exhibit resonance between structures of types (III), (IV), and (V).



Incursion of structures of type (V) will give rise to incipient ionisation of the side-chain bromine and to a positive charge on the benzyl residue, so that the molecule is predisposed to attack by nucleophilic reagents. The more important structures of type (V) become in the resonance hybrid, the more facile should be the nucleophilic substitution, and such substitutions should therefore be facilitated by electron-release substituents in the benzene ring. This is best understood if their effects on the initial and transition states is considered (using a tertiary base as the nucleophilic reagent and X as the electron-release substituent).

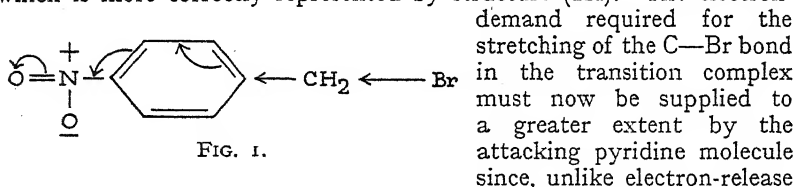
¹⁰ Cf. Baker, *J.C.S.*, 1932, 2634; 1933, 1129; Baker and Nathan, *ibid.*, 1935, 1840, for earlier statements of such a view.

¹¹ Brockway and Palmer, *J. Amer. Chem. Soc.*, 1937, 59, 2181.



In the initial state the permanent, mesomeric (polarisation) electron-release by X will lower the energy level, and hence tend to stabilise the molecule by increasing the importance of structures (IV) and (V), since it will provide increased distribution of the positive charge by the inclusion of new structures of the type $\overset{+}{X}=\text{C}_6\text{H}_4=\text{CH}_2\text{Br}$ in the resonance hybrid. In the transition state the stretching of the C—Br bond requires an increased supply of electrons (reckoned in terms of dipole moment, *i.e.* charge \times distance). Some of these come from the approaching pyridine molecule, but an increased supply is also available from the aryl group, since the electromeric (polarisability) electron-release of X is now called into play. The total electron-release by the group X should thus be greater in the transition complex than in the initial state, so that the energy level of the transition complex is lowered (by the introduction of X into the parent benzyl bromide) to a greater extent than in the initial, ground state. The potential energy of activation will thus be decreased and the reaction proceed with increased velocity.

Introduction of an electron-attracting group such as *p*-NO₂ will decrease the proportion of canonical structures of types (IV) and (V) in the resonance hybrid of the ground state of *p*-nitrobenzyl bromide, which is more correctly represented by structure (III). The electron-



demand required for the stretching of the C—Br bond in the transition complex must now be supplied to a greater extent by the attacking pyridine molecule since, unlike electron-release groups, the *p*-nitro-group has no means to supply electrons by an electromeric (polarisability) effect. In fact, the only possible electromeric effect would be in a direction further to deplete the electron supply at the side-chain C—Br bond (Fig. 1), and would thus not be called into play. The electron-attraction of the nitro-substituent will, however, by increasing the positive character of the side-chain methylene carbon atom (relative to that in benzyl bromide itself), reduce the energy needed for the approach of the pyridine molecule and so facilitate the necessary electron-supply in the transition complex from this source. It is difficult to forecast the total, overall result of these two conflicting effects on the energy supply to the C—Br bond, but the experimental result (slightly decreased velocity, *i.e.* increased energy of activation) shows that the difference in energy levels between the initial and transition states is rather larger in the *p*-nitro-derivative than in benzyl bromide itself.

In the *p*-nitrobenzyl bromide the resultant "tightening up" of the C—Br bond renders it more comparable to an aliphatic C—Br bond and,

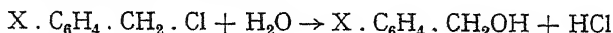
with increasing electron-attraction away from the side-chain, the electron supply necessary for the breaking of this bond must be supplied to a greater and greater extent by the attacking pyridine molecule and so, to a greater extent than before, energy is consumed and electrons are displaced in changing the position of the pyridine unit. A point may ultimately be reached when the positive charge on the methylene carbon, due to greatly increased nuclear electron-attraction, becomes so large that the energy necessary for the approach of the pyridine is greatly reduced and an actual decrease in the activation energy of the substitution reaction occurs. This is found to be the case, the velocity of reaction of 2 : 4-dinitrobenzyl bromide with pyridine being greater even than that of the *p*-methyl derivative. This incidence of a velocity minimum (here located at the *p*-nitro-compound) prior to the point of mechanistic change-over from the S_N2 to the S_N1 mechanism in a series where the structure of the attached group alters continuously in the direction of increasing electron-release, has been expressed in terms of energy surfaces by Hughes, Ingold and Shapiro.¹² The rather long gap between the minimum and the mechanistic change point is explained by the much greater plasticity in solution of the C—Br than of the C—N bond, and so it takes a large amount of "tightening-up" before the electrical needs of the forming and breaking bonds balance.¹³

In the hydrolysis of arylalkyl halides the benzyl group falls into the borderline S_N2 — S_N1 class¹⁴, and hence, to ensure reaction by an uncomplicated bimolecular mechanism, the Menshutkin reaction with these halides was studied in dry acetone, the low ionising power of which, in agreement with theory, suppresses any tendency to reaction by the unimolecular mechanism.¹⁵ The theoretical deductions are fully substantiated by the data^{15, 16} in Table I.

TABLE I.—VALUE OF SECOND ORDER REACTION COEFFICIENTS FOR THE REACTION BETWEEN $XC_6H_4 \cdot CH_2Br$ AND C_5H_5N (BOTH 0.025 M) IN DRY ACETONE AT 20°.

$X = 2 : 4-(NO_2)_2 > p-NO_2 < H < \{p-Cl < p-Br < p-F = p-I\} <$								
$10^4 k_1 =$	2.29	1.12	1.22	1.27	1.30	1.48	1.48	
$X = \{p-Bu \approx p-Pr > p-Et < p-Me\} < 2 : 4-Me_2$								
$10^4 k_1 =$	1.65	1.63	1.81	2.02	6.29	1/g. mol.-sec.		

The significance of the order of halogen and alkyl groups amongst themselves is referred to later. Bennett and Jones¹⁷ obtained a slightly different sequence for the reaction



in 50 % acetone at 69.8°, viz.—

$X = p-NO_2 < m-NO_2 < (m-Br, I, Cl, F) < (o-I, Br, Cl, F) <$									
$10^4 k_1 =$	0.706	0.782	1.32	1.43	1.56	1.59	1.70	1.70	1.94
$X = (p-I, Br, Cl) < H < p-F \ll p-Me$									
$10^4 k_1 =$	2.96	3.10	3.94	6.71	11.4	61.4			

The main difference is in the position of the halogen groups, but it would seem possible that, in the highly aqueous solvent employed and

¹² J.C.S., 1936, 228.

¹³ Professor C. K. Ingold, *private communication*.

¹⁴ Cf. Hughes, *Trans. Faraday Soc.*, 1938, 34, p. 190 for references.

¹⁵ Baker, J.C.S., 1934, 987; Baker and Nathan, *ibid.*, 1935, 519.

¹⁶ Baker and Nathan, *ibid.*, 1935, 1840; Baker, *ibid.*, 1936, 1448.

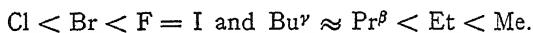
¹⁷ *Ibid.*, 1935, 1815.

with the low nucleophilic power of the attacking water molecule, some incursion of the unimolecular mechanism might be a complication. This view is rendered more probable (1) by the generally good agreement between the results and those of Oliver¹⁸ in 50 % aqueous alcohol, and (2) by the much greater velocity differences caused by strongly electron-attracting (NO_2) or release groups (Me), an aspect which is also revealed by the limited data for solvolysis of $p\text{-XC}_6\text{H}_4\cdot\text{CH}_2\text{Br}$ with 90 wt. % alcohol¹⁹ and for the reaction with pyridine¹⁸ in the same solvent, both at 30°.

	X = NO_2	H	Me
Solvolysis, 10^4k	= 0.21	2.0	8.19
Menschutkin, 10^4k	= 1.029	3.075	7.00

The lack of recognition of such mechanistic transitions effected by alterations in structure, solvents, etc., renders much of the earlier data valueless for the purpose of elucidating mechanism, a point already stressed by Hughes, Ingold, Masterman and McNulty²⁰ in connection with elimination reactions.

Some attention must now be given to the velocity orders of the halogens and alkyl groups amongst themselves. The positions of these groups in the velocity series clearly proves an overall electron-release capacity increasing in the order



The halogens have an order of inductive electron-attraction ($-I$) which decreases in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$ and Baddeley, Bennett, Glasstone and Jones²¹ have established the same order for their decreasing mesomeric electron-release ($+M$ effect). To explain the experimental order of electron-release the introduction of some other electron-release mechanism, varying in a different order, is necessary. The data would be satisfactorily explained if this were an electromeric electron-release ($+E$) decreasing in the order $\text{I} > \text{Br} > \text{Cl} > \text{F}$. Similarly, the classical inductive electron-release order for alkyl groups $\text{Me} < \text{Et} < \text{Pr}^\beta < \text{Bu}^\gamma$ requires the superposition of an electron-release mechanism decreasing in the order $\text{Me} > \text{Et} > \text{Pr}^\beta > \text{Bu}^\gamma$ to satisfy the experimental data. This second mechanism was postulated by Baker and Nathan²² to arise from partial conjugation of the electrons of the C—H bonds with an attached unsaturated atom or system, thus permitting tautomeric electron-displacement $\text{H}-\text{C}=\text{C}=\text{C}$. The effect of these various electron-displacements on the energy levels of the initial and transition states is most simply represented by a method already employed by the author²³ to interpret data for other side-chain reactions, *viz.*, by assigning purely arbitrary numerical values to each of them, and so obtaining a quasi-quantitative expression of their resultant effects on the energy of activation of the reaction. The energy levels in the unsubstituted compound are taken as reference standards. It must be emphasized that such arbitrary values (in unknown units) have no numerical significance except that their sign and relative magnitudes must be in agreement with

¹⁸ *Rec. trav. chim.*, 1922, 41, 646; 1923, 42, 516, 775.

¹⁹ Baker, *J.C.S.*, 1934, 987.

²⁰ Ref. 9, p. 908.

²¹ *J.C.S.*, 1935, 1827.

²² *Ibid.*, 1844; cf. Mullikan, Rieke and Brown, *J. Amer. Chem. Soc.*, 1941, 63, 41.

²³ Baker, *ibid.*, 1939, 1150; 1940, 692.

the known order (above) of electron-release (or attraction) by the various mechanisms. In the case of the tautomeric electron-release by alkyl groups there is the additional stipulation that, since this originates in the electrons of the C—H bonds which are directly conjugated with the unsaturated system, the magnitudes for CH_3 (3 such bonds), $\text{CH}_3 \cdot \text{CH}_2$ (2 bonds), $(\text{CH}_3)_2\text{CH}$ (1 bond) and $(\text{CH}_3)_3\text{C}$ (no bond) must decrease approximately in the ratios 3 : 2 : 1 : 0. Application of this method to the results for the Menshutkin reaction, which illustrates how the method may be applied to any side-chain reaction,* is made in Table II. The signs assigned to the arbitrary magnitudes are negative for electron-attraction ($-I$ effect) and positive for electron-release ($+I$, $+T$).

TABLE II.—RELATIVE ENERGY LEVELS IN THE REACTION
 $\text{XC}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{Br} + \text{C}_5\text{H}_5\text{N} \rightarrow \text{XC}_6\text{H}_4 \cdot \text{CH}_2 \cdot \overset{+}{\text{N}}\text{C}_5\text{H}_5\text{Br}$ IN DRY ACETONE AT 20°.

X	Ground State.			Transition State.				$E_g - E_a$ Reference Standard.
	I	M	Total (E_g).†	I^\ddagger	M	E	Total E_a .	
H	—	—	—	—	—	—	—	—
Cl	— 181	+ 21	— 160	— 180	+ 21	+ 2	— 157	— 3
Br	— 179	+ 19	— 160	— 178	+ 19	+ 4	— 155	— 5
F	— 186	+ 44	— 142	— 179	+ 44	0	— 135	— 7
I	— 153	+ 14	— 139	— 152	+ 14	+ 7	— 131	— 8
Bu $^\gamma$	+ 45	0	+ 45	+ 62	0	0	+ 62	— 17
Pr $^\beta$	+ 35	+ 8	+ 43	+ 40	+ 8	+ 12	+ 60	— 17
Et	+ 23	+ 16	+ 39	+ 26	+ 16	+ 24	+ 66	— 27
Me	+ 9	+ 24	+ 33	+ 10	+ 24	+ 36	+ 70	— 37

Hence a positive value for the total effect corresponds to a decrease in the energy level (increased stabilisation) and a positive value for the difference between the ground and activated states signifies an increase in activation energy for the reaction. This is clearly indicated in Fig. 1.

The values of $E_g - E_a$ thus predict activation energies decreasing in the order $\text{H} > \text{Cl} > \text{Br} > \text{F} \approx \text{I} > \text{Bu}^\gamma \approx \text{Pr}^\beta > \text{Et} > \text{Me}$, in agreement with the observed velocity sequence.

To complete the picture, the order $\text{Me} > \text{Et} > \text{Pr}^\beta > \text{Bu}^\gamma$ for the tautomeric electron-release by alkyl groups has been conclusively demonstrated by Hughes, Ingold and Taher⁶ in the unimolecular solvolysis of *p*-alkylbenzhydryl halides (*cf.* p. 634). Here the rate-determining stage is the unimolecular ionisation of the halogen, the transition state of which is so strongly favoured by the tautomeric type of electron-release from

* The method has also been applied to the cyanohydrin reaction with *p*-alkylbenzaldehydes where one set of relative energy levels so expressed accurately predicts the observed variations of both the equilibrium constant and the velocities of both the forward and back reactions with alteration of the alkyl substituent. (Baker and Hemming, *unpublished results*.)

† The actual figures are chosen to be of the order $10^3\mu$, where μ is the dipole moment of PhX in Debye units. In the series $\text{H} \rightarrow \text{Me}$, μ is actually 0, 1.69, 1.55, 1.43, 1.38, 0.70, 0.65, 0.58, 0.37. There is a theoretical reason why the deviations of the arbitrary values are larger for alkyl groups than for the halogens.

‡ $-I$ effects have been slightly decreased in the transition state because they are opposed to the increased polarisation of the C—Br bond and, for the converse reason, $+I$ effects have been considerably increased to take cognisance of the inductomeric effect.

the alkyl substituent (Fig. 3), that this effect is predominant and the "ideal" rate sequence $\text{Me} > \text{Et} > \text{Pr}^\beta > \text{Bu}^\gamma \gg \text{H}$ is well spaced and is supported by corresponding differences in Arrhenius critical energies.

FIRST ORDER RATE CONSTANTS AT 0° AND CRITICAL ENERGIES FOR THE HYDROLYSIS OF $p\text{-X} \cdot \text{C}_6\text{H}_4 \cdot \text{CHPhCl}$ IN 80 PER CENT. AQUEOUS ACETONE.

X = H	Me	Et	Pr ^β	Bu ^γ
$10^6 k_1 = 2.82$	83.5	62.6	46.95	35.9
$\bar{E} = 21.0$	18.9	19.4	19.8	20.05

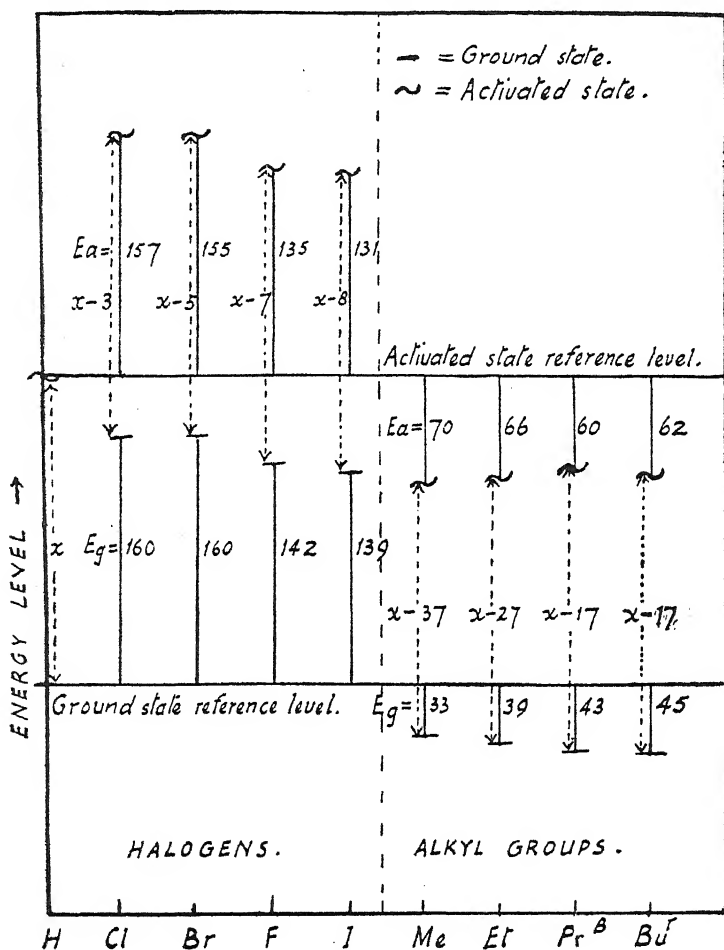
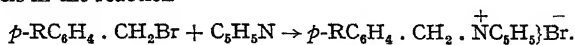


FIG. 2.

Energy levels in the reaction



This sequence would, of course, be predicted by assigning very much larger values to the E component of the alkyl groups in Table II. In passing, it might be noted that the almost instantaneous reaction of

p-methoxybenzyl bromide with pyridine²⁴ suggest that the strong + *T* effect of this substituent may transfer the mechanism to the *S_NI* region (Fig. 4).

(b) **Attack by a charged ion.**

When the attacking nucleophilic reagent is a charged anion it would be anticipated that the repulsive forces between

it and the benzyl halide would be greater than when it is a neutral molecule, *i.e.* the chemical inertia of the system would be greater. Hence the energy required to effect the close approach of the attacking

reagent might now become the more important factor and, if so, the facilitating effect of electron-attracting substituents might be greater.



FIG. 4.

Experimental evidence is in agreement with this view. Thus Baker and Nathan²⁵ obtained the following data in a study of the equilibrium $\text{XC}_6\text{H}_4 \cdot \text{CH}_2\text{Br} + \text{NO}_3^- \xrightleftharpoons[k_2]{k_1} \text{XC}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{NO}_2 + \text{Br}^-$ (the common cation being $\text{PhCH}_2 \cdot \text{NC}_5\text{H}_5$) in dry acetone at 20° and 40°.

	X = 2:4-(NO ₂) ₂	<i>p</i> -NO ₂	H	<i>p</i> -Bu ^v	<i>p</i> -Et	<i>p</i> -Me
$K^* = k_1/k_2 = 0.055$	0.105	0.176	0.189	0.170	0.189	
$10^4 k_1^{40^\circ} \sim 33$	8.2	4.3	6.8	7.1	8.81/g. mol. sec.	
$10^4 k_2^{40^\circ} \sim 613$	78	25.0	36.6	41.7	46.3 l./g. mol. sec.	

* *K* is independent of temperature within the range studied.

The values of both k_1 and k_2 are increased not only by *p*-alkyl and 2:4-(NO₂)₂, as in the Menshutkin reaction, but also by the weaker electron-attraction of a *p*-NO₂ substituent. When X = alkyl the ratios k_1^X/k_1^H and k_2^X/k_2^H are almost identical, indicating that the polar effect of these substituents affects mainly the energy required in stretching the C—Br or C—ONO₂ bond. When X = *p*-NO₂ and especially 2:4-(NO₂)₂, the values of k_2^X/k_2^H (3.1 and 24.5 respectively) are much larger than those of k_1^X/k_1^H (1.9 and 7.7) and this in spite of the fact that, with pyridine, benzyl bromide reacts > 200 times faster than benzyl nitrate under identical conditions. It would seem, therefore, that the polar effect of the nitro-substituents is concerned mainly with the energy requirements for the approach of the negative ion.*

The effect of substituents on *K* may be briefly noted. Whereas alkyl substituents hardly alter the position of equilibrium (the slight change being in favour of the benzyl nitrate) nitro-groups shift it largely in favour of the benzyl bromide. This is readily understood, since the presence of the group (Fig. 5) in the side-chain of benzyl nitrate would mean that nuclear nitro-substituents should exert a much greater destabilising effect on the ground state of the molecule than they would in the benzyl bromide.

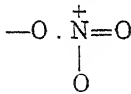


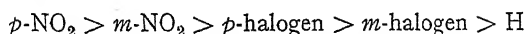
FIG. 5.

²⁴ Baker, *J.C.S.*, 1932, 2631; Lapworth and Shoesmith, *ibid.*, 1922, 121, 1391.

²⁵ *Ibid.*, 1936, 236.

* Orientation effects depending on the spherical nature of the bromide ion and the planar configuration of the degenerate nitrate ion may also play a part. This aspect is discussed in the communication cited above.

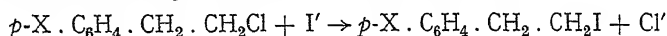
The facilitating effect of electron-attracting substituents (on velocity) is also shown in the attack by iodide ion on substituted benzyl chlorides. Bennett and Jones²⁶ found the order



(Me not examined) for the second order k^{200} in dry acetone.

3. On β -Phenylethyl Halides.

In this class no conjugation between the aromatic nucleus and the side-chain halogen is possible, and the energy for the rupture of the C—Cl bond (largely resembling an aliphatic C—hal bond) must be supplied mainly by the attacking nucleophilic reagent. The reaction should thus be facilitated by even weak electron-attracting substituents and electron-release by the tautomeric mechanism should be unimportant. The data of Baddeley and Bennett²⁷ for the reaction :



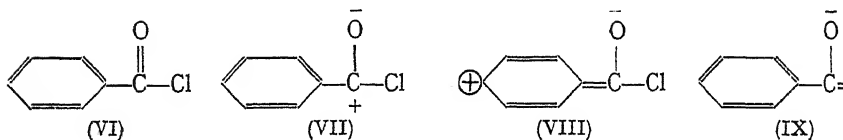
in dry acetone at 75° substantiate these conclusions :

X = NO ₂	F	Cl	Br	I	OMe	H
2nd order $k = 3.76$	1.55	1.65	1.63	1.40	1.04	0.735

The accelerating influence of methoxyl, in spite of its very weak — *I* and powerful + *T* effect is especially significant.

4. On Benzoyl Halides.

The types of structure (VI)-(IX) will contribute towards the ground state of the benzoyl chloride molecule.



The hydrolysis of acid chlorides is not catalysed by hydron,²⁸ but in alkaline solution it is too rapid for measurement. The attack of OH' or H₂O (and, by implication, of any nucleophilic reagent) is thus at

positive carbonyl carbon, the transition complex (for the benzoylation of amines) being of the type (Fig. 6). Incursion of structures of type (VIII) (arising from conjugation of the aromatic nucleus with the carbonyl group) will stabilise the molecule against attack by a nucleophilic reagent. Introduction of electron-release substituents would further increase the importance of type (VIII) structures and would stabilise them to a greater extent than it does the transition complex (in which conjugation of CO with the nucleus is partially destroyed), but electron-attracting nuclear substituents, by providing an alternative conjugation with the aromatic nucleus, should decrease the importance of (VIII) and increase that of (VII). Hence

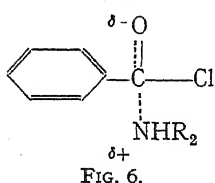


FIG. 6.

²⁶ J.C.S., 1935, 1815.

²⁷ Ibid., p. 1819.

²⁸ Velasco and Ollero, *Anal. Soc. Espan. Fisquim.*, 1936, 34, 179; 1937, 35, 76. Oliver and Berger, *Rec. trav. chim.*, 1927, 46, 609.

the latter type of substituent should facilitate the reaction. The results of Williams and Hinshelwood²⁹ for the benzoylation of anilines in benzene and those of Norris, Fasce and Staud³⁰ for the interaction of benzoyl chlorides with excess ethyl alcohol, confirm these deductions.

SECOND ORDER VELOCITY COEFFICIENTS FOR THE REACTION $\text{XC}_6\text{H}_4 \cdot \text{CO} \cdot \text{Cl} + \text{NH}_2\text{C}_6\text{H}_5 \rightarrow \text{XC}_6\text{H}_4 \cdot \text{CO} \cdot \text{NHC}_6\text{H}_5 + \text{HCl}$ IN BENZENE AT 25°.

X = <i>p</i> -Me	H	<i>p</i> -Cl	<i>p</i> -NO ₂
10 ² <i>k</i> = 3.91	6.88	10.4	58.1
E = 7800	7350	7000	5900

RELATIVE VALUES OF FIRST ORDER VELOCITY COEFFICIENTS FOR THE REACTION $\text{XC}_6\text{H}_4 \cdot \text{CO} \cdot \text{Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{XC}_6\text{H}_4 \cdot \text{CO} \cdot \text{OC}_2\text{H}_5 + \text{HCl}$ IN ETHYL ALCOHOL AT 0°.

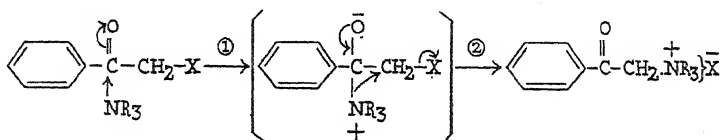
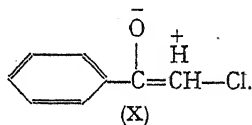
X = <i>p</i> -NO ₂	<i>m</i> -NO ₂	<i>p</i> -Cl	<i>p</i> -I	H	<i>m</i> -OMe	<i>p</i> -OMe	<i>m</i> -Me	<i>p</i> -Me
Rel. <i>k</i> = 21.6	20.5	1.9	1.9	(1)	1.1	0.81	0.85	0.78

In the former reaction, in accord with the suggestion that the main energy requirement is that for the electrostriction of the attacking reagent, the energy of activation is greater the weaker is the nucleophilic power (basic strength) of the attacking base. Thus, for the benzoylation of various substituted anilines $\text{Y C}_6\text{H}_4\text{NH}_2$ the data are²⁹

Y = <i>p</i> -Me	H	<i>p</i> -Cl	<i>m</i> -NO ₂	<i>p</i> -NO ₂
10 ² <i>k</i> ^{25°} = 29.8	6.88	1.50	0.044	0.0042 l./g. mol.-sec.
E = 6800	7350	7600	10,500	11,800

5. On Phenacyl Halides.

Attack of a nucleophilic reagent on a phenacyl halide might, theoretically, occur directly at the side-chain methylene carbon (as in β -phenyl-ethyl halides) or at carbonyl carbon (as in benzoyl halides). Resonance in the ground state of a phenacyl halide would be expected to occur between structures exactly similar in type to (VI), (VII), and (VIII) already given for benzoyl halides, whereas (IX) would be replaced by the structure (X). It would therefore seem that there is at least a *prima facie* case for assuming that, as with the benzoyl halides, the initial attack of the nucleophilic reagent is at carbonyl carbon. The formation of a phenacyl-pyridinium halide would be represented thus:—



in which (1) is the rate-determining stage, and (2) represents a rapid intramolecular rearrangement of the type termed by Ingold and Shoppee,³¹ "pinacolic electron-displacement," and familiar in rearrangements of the pinacol-pinacolone type. The following evidence supports this view of the reaction mechanism.

²⁹ J.C.S., 1934, 1079.

³⁰ J. Amer. Chem. Soc., 1935, 57, 1415.

³¹ J.C.S., 1928, 365.

(1) As with the benzoyl halides, the reaction with pyridine is bimolecular, and is facilitated by the introduction of electron-attracting groups and retarded by electron-release groups.³²

SECOND ORDER VELOCITY COEFFICIENTS FOR THE REACTION $X \cdot C_6H_4 \cdot CO \cdot CH_2Br$

$+ C_5H_5N \rightarrow X \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot \overset{+}{N}C_5H_5 \cdot Br$, BOTH 0.025 M, IN DRY ACETONE AT 20°.

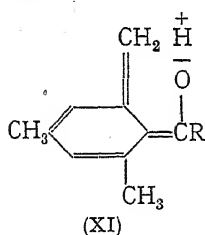
X = <i>p</i> -NO ₂	<i>p</i> -Br	<i>p</i> -Cl	H	<i>p</i> -Me	<i>m</i> -Me	<i>o</i> -Me	<i>p</i> -Bu'	2:4-Me ₂	2:4:5-Me ₃	2:4:6-Me ₃
10 ³ k = 1.9	1.71	1.29	0.79	0.74	0.64	0.55	0.57	0.50	0.54	~10 ⁻⁴
										l./g. mol.-sec.

(2) Thomson and Stevens³³ found that phenyl bromomethyl sulphone, $Ph \cdot \overset{+}{S} \overset{+}{O}_2 - CH_2Br$, does not react with either benzyldimethyl-aniline

or piperidine. The sulphone group $\overset{+}{S} \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$ is well able (by its — I

effect) to activate the adjacent methylene group towards direct nucleophilic attack, but is unable to accommodate the type of tautomeric polarisation present in the carbonyl group $C \equiv \overset{+}{O}$, which would thus seem to be essential to the mechanism.

(3) The "Ortho-effect."—It will be noticed that, in the pyridine reaction, the retarding effects of methyl substituents in the 2:4- and 2:4:5- positions are of magnitudes anticipated from the effects of single methyl substituents, but in the 2:4:6-trimethyl-derivative (with two substituents ortho to the side-chain) the reaction velocity becomes too slow for accurate measurement. Further investigations³² (unpublished) have shown that such retardation is partly spatial (applicable only if the attack is at the CO and not at the more distant CH₂ group) but partly, also, due



to the incursion of structures of the type (XI) in 2:4:6-trimethylacetophenone ($R=CH_3$) and its halides ($R=CH_2X$). The increased resonance in 2:4:6-trimethylacetophenone relative to the 2:4:5-isomeride has been demonstrated by its slightly lower heat of combustion (0.17 volt-electron per mol.), its higher molecular refractivity, and the much lower basicity of its carbonyl oxygen. These results have important bearings on the whole problem of the "proximity" or "ortho-effect,"³⁴ but limitations of space prevent further discussion here.

It is recognised that this survey has omitted all reference to many and important types of side-chain substitution, and to various interesting aspects of the problem, but it was considered that the more detailed examination of the series chosen would best illustrate the usefulness of the method of energy level treatment in the elucidation of side-chain reaction mechanism.

The University,
Leeds.

³² Baker, J.C.S., 1938, 445; Baker and Tweed, unpublished results.

³³ *Ibid.*, 1932, 70.

³⁴ Cf. *inter alia*, Dippy, Evans, Gordon and Watson, J.C.S., 1937, 1421.

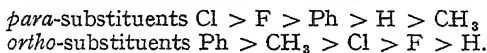
GENERAL DISCUSSION

Dr. D. P. Evans (*Cardiff*) said: The energy level treatment suggested by Baker will no doubt yield much useful information regarding side chain reactions in which the variable substituent is far removed from the seat of reaction, *e.g.* *m* and *p* substituted benzene derivatives. The influence of such groups upon the reactivity of the side chain appears to originate entirely in the usual polar effects (inductive, inductomeric, mesomeric and electromeric), which cause changes in activation energy but no alteration of the *P* factor in the equation $k = PZe^{-E/RT}$.

When the variable substituent is in close proximity to the reaction centre, *e.g.* *ortho*-substituted benzene derivatives and substituted acetic acids and esters, simultaneous changes in *E* and *P* occur owing to local disturbances which in all probability do not have their origin in the usual polar effects of the substituents, and cannot be explained on the simple Victor Meyer steric hindrance principle. In such cases it seems unlikely that an explanation of the changes in activation energy may be expected from the influence of the inductive, inductomeric, mesomeric or electromeric effects of the substituent groups. As an example of the differences caused by varying (a) the *para*-substituent and (b) the *ortho*-substituent we have the following results for the addition of methyl iodide to dimethylanilines in methyl alcohol.¹

<i>p</i> -subst.	<i>E</i> (cal.)	<i>o</i> -subst.	<i>E</i> (cal.)	P_{ortho}/P_{para}
H	15,200	H	15,200	1
Me	14,500	Me	21,100	250
Ph	15,400	Ph	21,600	400
Cl	16,200	Cl	19,900	40
F	15,500	F	16,300	1

The effects of the substituents are quite different in the two positions, *e.g.* the activation energies decrease in the series



Moreover in all cases except for fluorine the *P* factor is considerably higher for the *ortho* than for the corresponding *para* compound.

Again for the addition of methyl iodide to dialkylanilines in methyl alcohol² the results shown in Table I. have been obtained. Here the variable substituents are alkyl groups situated near the seat of reaction and it seems very probable that the high activation energies for the diethyl, ethyl propyl, dipropyl and dibutyl compounds are not due to the usual polar effects of these groups. Steric effects are obviously present, but only when the two groups attached to the nitrogen are larger than methyl. Baker and Nathan's ideas are not applicable here since the system is saturated.

TABLE I.

Alkyl Groups.	<i>E</i> (cal.)	Log <i>PZ</i>
Me ₂ . .	15,200	6.9
Me . Et .	15,400	6.9
Me . n-Pr .	15,400	6.7
Et ₂ . .	18,000	7.7
Et . n-Pr .	19,000	8.2
n-Pr ₂ . .	19,000	8.0
n-Bu ₂ . .	20,000	8.7

These results have been put forward to support the suggestion that the influences of groups situated near the reaction centre cannot be fully

¹ Evans, Watson and Williams, *J. Chem. Soc.*, 1939, 1345, 1348.

² Evans, *Unpublished results*.

explained in the light of the usual polar effects. The above results, however, receive a possible interpretation on the postulate of an interaction (in the transition complex) between the reaction centre and the variable grouping, a theory which has been developed in several papers from Watson's laboratories.

Another example where the variable substituent stands near the seat of reaction is the acid-catalysed bromination of alkyl phenyl ketones.³ Here there is a large rise in both *E* and *P* in passing from acetophenone to propiophenone which has been interpreted as being due to hydrogen bond formation between β -C and carbonyl oxygen in the transition complex.^{3, 4} In 1939, however, Baker⁵ suggested that the high *E* for propiophenone was due mainly to the effect of the additional methyl on the conjugation of the hydrogens of the methyl group present in acetophenone. The change in *P*, however, indicates the operation of some factor other than the usual polar effects of the alkyl substituent, and on these grounds I suggest that for this reaction Baker's explanation does not afford a complete interpretation of all the observed facts. Further evidence for this suggestion is found in the following. If the high activation energy for propiophenone is due entirely to alkyl conjugation with carbonyl, then for similar reasons the activation energies for the acid catalysed prototropy of methyl ethyl and methyl tert-butyl ketones should be higher than that for acetone under the same conditions. Experiment⁶ shows that the activation energies for these three compounds are almost identical (Table II.). The presence of the bulky phenyl group conjugate with carbonyl in propiophenone gives

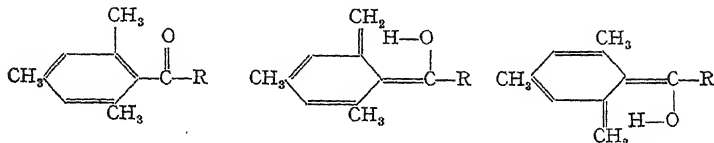
TABLE II.

BROMINATION OF R. CO. Me IN 50 %
ACETIC CONTAINING 0.5 M-HCl.

R.	E.	Log PZ.
Me . . .	19,700	10.2
Et . . .	20,000	10.4
Bu ^v . . .	19,500	9.6

the molecule that degree of rigidity which is necessary for the formation of the hydrogen bond, whereas no similar restriction of rotation exists in the aliphatic ketones.

In the reaction between phenacyl bromides and pyridine the inadequacy of alkyl conjugation as an explanation of the marked inhibition of reactivity in the 2:4:6-trimethylphenacyl bromide is admitted by Dr. Baker. It is significant that a very low speed of reaction is found only when two methyl groups stand *ortho* to carbonyl; a fact which indicates (as Baker has suggested) the operation of some spatial effect. Would not this latter effect be interpreted as a greater probability for hydrogen bond formation in the transition complex involving the structures



This postulate of actual hydrogen bond formation requires a special spatial arrangement of the *o*-methyl and carbonyl oxygen which is more probable in the 2:4:6-compound than in the 2:4:5-, the 2:4- or the 2-methyl derivatives because there is always a methyl group near the CO.

Dr. J. W. Baker (*Leeds*) said: In reply to Frank: Hughes and Ingold⁷ have stressed the difficulties which may arise when either of the parameters in the Arrhenius relationship is regarded as an index of the effect

³ Evans, *J. Chem. Soc.*, 1936, 785.

⁴ Evans and Gordon, *ibid.*, 1938, 1434.

⁶ Evans, *Unpublished results*.

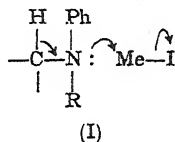
⁵ *Ibid.*, 1939, 1150.

⁷ *This vol.*, p. 671.

of structural changes on reactivity. In the bimolecular, nucleophilic substitutions studied, the substituent is so placed that, although its effect is transmitted to the site of the reaction through a connecting conjugated system, it is sufficiently distant to eliminate any possibility of "proximity" effects. Since the extreme range of velocity and critical energy differences is small the rate-constants themselves have been taken as a true indication of the corresponding differences in energy levels in the initial and transition states of the reaction, *i.e.* of the potential energies of activation.

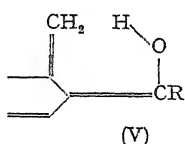
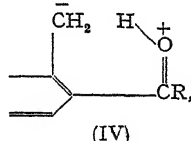
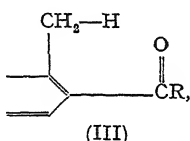
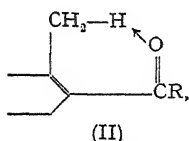
In reply to Evans: The object of this communication is to show that treatment based on changes in energy levels caused by the polar effects of a substituent on the electron distribution in the initial, transition and final states of a reaction often provides an adequate explanation of the changes in reaction velocity or position of equilibrium, without the introduction of other hypotheses such as the hydrogen bonding proposed by Evans. It does not exclude the latter as possibly operative in addition.

In the reaction between dialkylanilines and methyl iodide, contrary to the contention of Evans, tautomeric effects of alkyl groups in the dialkylaniline may be operative since the α -C—H bonds are conjugated with the unshared electron pair of unsaturated, tercovalent nitrogen: *e.g.* in the transition complex (I).

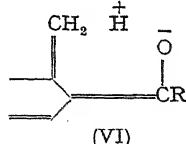


The results do suggest that some factors, other than the electron-release effects of the alkyl groups, are operative in this reaction. Differences in the energies of solvation of the various cations may influence the activation energies in the solvent used.

The hydrogen bond between carbonyl oxygen and the *ortho*-methyl groups in 2:4:6-trimethylacetophenone, proposed by Evans, is essentially the same phenomenon as that described in this paper. The structure (II) arises from resonance between structures of the types (III) to (VI)

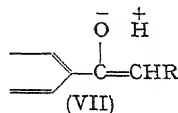


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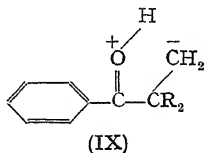
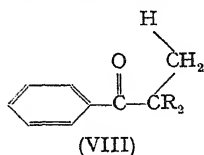
and the greater resonance energy (0.17 e.volts) of 2:4:6- than of 2:4:5-trimethylacetophenone is adequately explained by the fact that nine C—H bonds are involved in the former, and only six, in the latter compound. In the reactivity of the phenacyl halides, the results suggest that, *over and above this factor*, a purely spatial effect is superposed.

In the phenyl alkyl ketones it is suggested that the combined inductive and tautomeric effects of the alkyl groups (the latter arising from the inclusion of structures of the type (VII) in the resonance hybrid) are likely to be more important than hydrogen bonding with the β -hydrogen atom, especially since the experimental data receive an adequate explanation on the basis of the former hypothesis alone.⁸ It should be noted that the β -hydrogen bonding of Evans is in

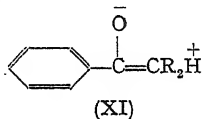
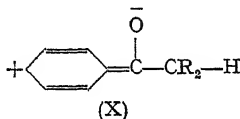


⁸ Cf. Baker, *J.C.S.*, 1939, 1154.

a somewhat different category to the conjugation of α -C—H bonds with the carbonyl group. The β -C—H bonds are not conjugated with the carbonyl group and any such β -hydrogen bonding can arise only from limited resonance between the structures (VIII) and (IX) which represent a five-membered chelate ring.



The greater rigidity of the phenyl alkyl ketones, postulated by Evans, probably arises from the partial double bond character of the link between the aromatic nucleus and carbonyl-carbon due to structures of the type (X) which will be of greater importance owing to the greater degree of conjugation between phenyl with carbonyl than between methyl and carbonyl. Structures of type (X) might conceivably, in turn, increase the



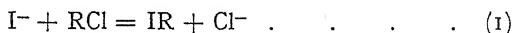
importance of structures of type (XI) and thus explain the greater importance of the tautomeric effects of the alkyl group CR_2H in the phenyl alkyl ketones than in the methyl alkyl ketones.

ACTIVATION ENERGY OF IONIC SUBSTITUTION.

BY E. C. BAUGHAN AND M. POLANYI.

Received 2nd September, 1941.

(1) The theory of the activation energy of "negative substitution" of the type



was first put forward provisionally in very simple terms.¹ It was suggested that the activation energy corresponds to the energy required for such an extension of the RCl bond as would allow the Cl atom to be replaced by the larger Cl^- ion. For the back reaction it would be equal to the energy of extension of the RI bond to the point at which I could be replaced by Cl^- . This theory was finally established by Ogg and Polanyi by detailed calculation in which it seems to have lost some of its usefulness by becoming rather complex.² The purpose of this paper is to show that a very simple form of the theory—almost as simple as the original one—can be used in certain cases with good approximation, and that this has even the advantage of avoiding certain mistakes which have crept into the detailed calculation mentioned above.¹

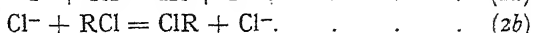
¹ Polanyi, *Proc. Roy. Soc., B*, 1934, **116**, 203.

² Ogg and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 604.

The cases to which the proposed simplification applies are the symmetrical negative substitutions of the type



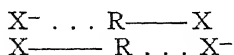
or



The limitation to these symmetrical cases does not greatly impair the usefulness of our investigation. Though the available experimental material concerning the rate of such reactions is small and cannot be easily expanded, yet there is a close parallelism between the rates of the symmetrical reactions and those of allied unsymmetrical reactions which can be easily measured. The rates of the reactions 2a and 2b for example, are closely related to those of the forward and back directions of the unsymmetrical reactions 1. The rates of both the latter reactions lie intermediate between those of 2a and 2b; and moreover it can be safely assumed (on theoretical grounds confirmed by experimental indications) that changes in the nature of R would cause parallel changes in both the symmetrical and the unsymmetrical reactions in question. Any theory of symmetrical ionic exchanges would therefore also comprise the essential elements of the theory of unsymmetrical ionic substitutions.

(2) Our simplified theory is based on a qualitative result of the calculations of Ogg and Polanyi² which it accepts as correct. It is a principle of this calculation to neglect at first the resonance energy in the transition state and its neighbourhood, assuming that the resonance energy in an ionogenic reaction is comparatively small (on account of the profound electronic rearrangement involved in it) and that hence the upper limit of the activation energy, obtained by neglecting the resonance will be only slightly in excess of the true value. This principle leads to a "crossing" of the energy surfaces relating to the initial and the final chemical states, and for symmetrical ionic exchanges the crossing will occur along a curve lying in the diagonal plane of the usual three dimensional energy diagram of the reaction. Neglecting resonance, the transition state is represented by the lowest point of the curve. The simplified theory presented here consists in determining this curve (and its lowest points) directly, without plotting the energy surfaces of which it forms the crossing line.

Resonating systems of the type

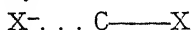


can be symmetrical only if R itself is symmetrical. If R is a carbon radical it has to be flattened out with its three valencies in one plane. But this will not result in complete symmetry unless the substituents attached to these valencies themselves possess a plane of symmetry. Assuming this to be the case we note that: (1) a certain amount of energy might be required to bring the radical into a plane, especially if the substituents attached to it are voluminous; (2) the forces of attraction and repulsion between R and X as well as between R and X⁻ are modified by the flattening of the radical. There is (a) repulsion between X⁻ and the three substituents of the central carbon atom of R; (b) repulsion between these substituents and X which modifies the bond energy R—X. "Steric hindrance" caused by voluminous substituents linked to the central carbon atom of R may be considered as the sum of the increments to the activation energy indicated above

under 1, 2*a* and 2*b*. No attempt will be made here to calculate these terms and our consideration will therefore remain incomplete so far as cases are concerned in which there is an appreciable steric effect. This proviso covers also such cases in which one or more of the substituents attached to the central carbon possess no plane of symmetry, since the consequent deviation of the distances $X^- \dots C$ and $C-X$ from equality in the transition state will be noticeable only if the substituents attached to C exercise a steric hindrance; otherwise the lack of symmetry in the substituents does not matter.

The procedure thus outlined for the calculation of the activation energy of symmetrical ionic substitutions takes no account of the solvent in which the reaction takes place. It will be shown later that owing to a compensation of the effects of the various simplifications involved in this procedure we may expect it to yield an activation energy which is not appreciably different from the activation energy in solution.

(3) In the symmetrical system



there is repulsion between X^- and C for all distances *a* and attraction between C and X for distances greater than the normal nuclear separation of the C—X bond. Since we will not deal here with small distances, we may refer to the two interactions as the repulsion energy *R* acting between X^- and C, and the molecular attraction energy *M*, acting between C and X. We are seeking the value of *a* for which *R* + *M* is at a minimum and wish to establish this minimum value. From the condition

$$\frac{\partial R}{\partial a} = - \frac{\partial M}{\partial a} \quad (3)$$

it follows that in the transition state the forces acting on X^- and X are equal and opposite; the force of extending the bond C—X is equal to the force pressing the ion X^- into C, while the nuclear distances are equal on either side.

The solution of this problem requires therefore the knowledge of two facts (*a*) the extension of the bond necessary and (*b*) the potential energy of the C—X bond as a function of distance which also gives the necessary forces for equation (3). As a first approximation we shall consider the ionic radius of X^- as incompressible; on this view the activation energy is simply the energy necessary to extend the C—X bond until it has the length corresponding to a C atom and an X^- ion in contact. For this we must know the ionic radius of X^- ; the C—X distance in the original unstretched bond is well known from electron diffraction experiments.³

(*a*) Ionic radii from crystal lattices have been given by Pauling.³ From his data come the following results:

Na^+ 0.95, K^+ 1.33, Rb^+ 1.48, Cs^+ 1.69; Cl^- 1.81, Br^- 1.95, I^- 2.16 Å.

From these results we should expect the interatomic distances for the alkali halide ion pairs in the gas phase which are given in the first row of Table I. These distances have, however, been measured directly by electron diffraction methods;⁴ the results are given in the second row of Table I. It can be seen that these observed distances are considerably smaller than the sum of the crystal radii. The ionic radii

³ Pauling, *The Nature of the Chemical Bond*, Cornell University Press, 1939.

⁴ Maxwell, Hendricks and Mosley, *Physic. Rev.*, 1937, **52**, 968.

TABLE I

	NaCl	NaBr	NaI	KCl	KBr	KI	RbCl	RbBr	RbI	CsCl	CsBr	CsI
Calc. (Pauling)	2.76	2.90	3.11	3.14	3.28	3.49	3.29	3.43	3.64	3.50	3.64	3.85
Observed	2.51	2.64	2.90	2.79	2.94	3.23	2.89	3.06	3.26	3.06	3.14	3.41
Calc. (This paper)	2.48	2.61	2.79	2.81	2.94	3.12	2.93	3.06	3.24	3.09	3.22	3.40

are therefore smaller in the isolated molecule than in the crystal. Since large ions are more compressible, we have assumed that this shortening is to be divided among the two ions in a salt in the ratio of their crystal radii. From this assumption we obtain the radii

$\text{Na}^+ 0.87$, $\text{K}^+ 1.20$, $\text{Rb}^+ 1.32$, $\text{Cs}^+ 1.48$; $\text{Cl}^- 1.61$, $\text{Br}^- 1.74$, $\text{I}^- 1.92$ A.

The third column of Table I gives the interatomic separations calculated as the sum of these new radii; except for sodium and potassium iodides the agreement is fairly good.

These new radii refer to the ions *in vacuo*, those of Pauling to the ions surrounded by the alternating array of ions in the lattice. The values appropriate to the present calculations would refer to ions embedded in the solvent. An exact calculation of these radii is a very complex matter. But as the covalent and Van der Waals forces are of such short range compared with the Coulomb force, and the covalent and Van der Waals radii of atoms vary but slightly, the *vacuo* values are the more nearly appropriate to this question. For the covalent atoms Pauling gives the radii $\text{Cl } 0.99$, $\text{Br } 1.14$, $\text{I } 1.33$; to replace these by ions of "vacuo" radii needs an extension of the bond by 0.62, 0.60, 0.59 respectively. We shall adopt the mean 0.60; a correction for the expansion of the bond from room temperature to 1200°C . (the temperature of the electron diffraction measurements) would shorten this to 0.58 A.

Hence our problem at this approximation reduces to that of finding the energy necessary to extend the carbon halogen bond by 0.58 A.

(b) The calculation of the potential energy curve must be made from the observable data on the vibration frequencies, ν , interatomic separations r_0 , and dissociation energies D of the bonds. Of these quantities the first two are well known, and for the last we have adopted the values given by us elsewhere.⁵ The potential energy curves were then calculated from the approximation equation of Morse:

$$V = D(2e^{-a(r-r_0)} - e^{-2a(r-r_0)}). \quad (4)$$

The data used are given in Table II.

In a recent publication, Linnett⁶ has recommended another empirical equation for the potential energy curve of a diatomic molecule:

$$V = \frac{a}{r^m} - be^{-nr}. \quad (5)$$

⁵ Baughan and Polanyi, *Nature*, 1940, 146, 685.

⁶ Linnett, *Trans. Faraday Soc.*, 1940, 36, 1123.

TABLE II.—DATA FOR MORSE CURVES.

	D K.cals.	ν Cm ⁻¹ .	r_0 (A.).	a (A.) ⁻¹ .
$\text{CH}_3\text{—Cl}$	83.5	710	1.76	1.66
$\text{CH}_3\text{—Br}$	70.6	594	1.91	1.63
$\text{CH}_3\text{—I}$	55.8	522	2.10	1.66

This has the merit that it explains the empirical relation found between the force constants and equilibrium distances for the different links formed by a given pair of atoms. In this equation a , m , b and n are constants which have to be determined in each case; by giving m the value 3 recommended by Linnett, the other three can be deduced from the observables mentioned. This curve was calculated for the case of methyl iodide, the appropriate equation being:

$$V \text{ (k.cal.)} = \frac{2895}{r^3} - 4692 e^{-1.212r} \quad (5')$$

(where r is in A.). The comparison of this curve with the Morse curve is shown in Table III. It can be seen that at no point in the range

TABLE III.—COMPARISON OF MORSE AND LINNETT FUNCTIONS FOR $\text{H}_3\text{C} \dots \text{I}$.

Spacing A.	$V(\text{Morse})$ k.cal.	$V(\text{Linnett})$ k.cal.
1.70	50	43
1.80	23	15
1.90	9	8
2.00	2	1
2.10	0	0
2.20	1	1
2.30	5	4
2.40	9	8
2.50	14	13
2.60	18	19
2.70	22	24
2.80	26	29
2.90	30	34
3.00	34	38
3.10	37	42
3.30	42	50

(Zero of energy = V_{r_0} ; values rounded off to nearest k.cal.)

C—X bond by the same amount so that the sum of ionic compression and bond extension retains its value:

$$c + e = 0.58 \text{ A.} \quad (6)$$

Estimates for c and e can be obtained by reference to the conditions of equal and opposite forces stated in equation 3. It is not easy to assess the "ionic compressibility" in our particular case; we have to estimate the repulsion energy as a function of the nuclear separation between the ion X^- and the central carbon atom. We may regard it as a function of the reduction c of the nuclear separation below the sum of the atomic and ionic radii and assume that it is the same as that arising between two neutral atoms X and C when their normal separation is reduced. Thus we identify the compression branch of the bond energy curve of C—X with R as a function of c . For example the repulsion between C and I^- is found from Fig. 1 by plotting c along the abscissa from right to left, starting at the normal nuclear separation of the C—I bond, and reading the energy values off the curve.

With this assumption, it is easy to derive the solution fulfilling the conditions (3) and (6). In the upper part of Fig. 1 we have plotted (in arbitrary units) the forces $\partial R/\partial a$ and $\partial M/\partial a$ which are identified

with which we are concerned is the difference more than two or three k.cal. Either approximation is therefore probably good to this accuracy. We have chosen that due to Morse.

From the extension 0.58 A. and the assumption of Morse's equation we obtain the values (which we call Q_1) CH_3Cl 31; CH_3Br 26; CH_3I 22 k.cal. The use of the crystal radii would give values 15, 10, 8 cal. higher respectively.

Taking into account the compressibility of the ions makes very little difference. Suppose the ion is compressed by the amount c then (to keep the configuration symmetrical) we have to reduce the extension (e) of the

with the first differentials of the Morse curve for the points in question; the forces are, of course, zero for normal nuclear separation, and of opposite sign on either side. Plotting c to the left and e to the right of the zero point of force the conditions

$$c + e = 0.58 \text{ and } \partial R / \partial a = -\partial M / \partial a$$

are seen to be jointly fulfilled by the end points of the two-headed arrow measuring 0.58 Å. We can then read R and M by projecting these points unto the lower half of the diagram. By this method we obtain

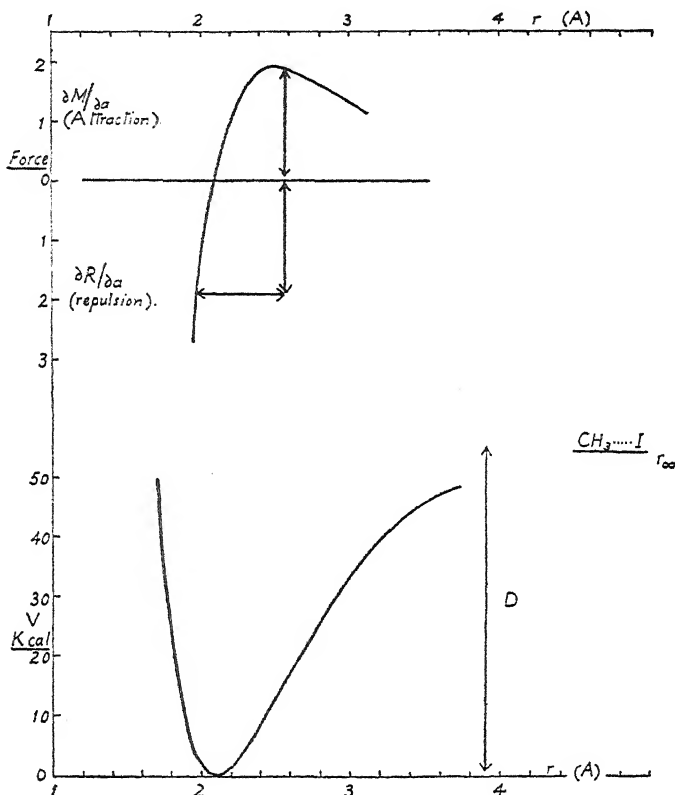


FIG. 1.

the values Q which are seen to differ slightly from Q_1 : X = Cl, Br, I; $Q = 28, 23, 19$.

(4) In order to assess the significance of these results we will anticipate here the conclusion drawn in the next section that the cohesive forces operating within the system of reacting particles, and between this system and the surrounding solvent, jointly cause only a small positive term (W) of about 1 k.cal. in the activation energy (q), which is expressed by

$$q = Q + W - U \quad (7)$$

where U stands for the resonance energy in the transition state. Adding 1 k.cal. for W to our Q_2 values we find that the $Q + W$ values show

a similar trend (29, 24, 20) to the experimental activation energies quoted by Ogg and Polanyi² (23, 19, 17), but are slightly higher (by 6, 5 and 3 k.cal. respectively for the Cl^- , Br^- , I^- cases). This excess may be due to the resonance energy U in the transition state, or to the inevitable uncertainties in this calculation; a reduction of the distance of stretch by only 0.03 would give quantitative agreement. These results therefore support our view that the resonance energy in the transition state is small; various approximate estimates for it give values of between 5 and 2 k.cal.

(5) There remains, to complete our argument, the task of assessing W , the total effect of the normal cohesive forces acting within the system $\text{X}^- \dots \text{C} \text{---} \text{X}$ and between this system and the solvents, of which we have said—in anticipation of the following calculation—that it amounts only to about 1 k.cal.

The following list of the "charging energies" $e^2/2r(1 - 1/D)$ of a Cl^- ion for $D = 80, 20, 7.5$ will be useful: 102, 98, 90 k.cal. respectively. The last two figures would apply to Cl^- in acetone and in CH_3Cl as a solvent. The difference of 8 k.cal. may be taken as a good measure of the heat accompanying the transfer of an ion Cl^- from a medium of pure acetone to a medium of pure CH_3Cl . Of this heat just about half, say 4 k.cal. will be due to the replacement of the acetone molecules immediately surrounding the ion by CH_3Cl molecules. If only one acetone molecule is replaced by a CH_3Cl molecule the heat effect will be, say, one-fourth of this energy, i.e., 1 k.cal. if the co-ordination number is 4, and less if it is more than 4. Thus it follows that the energy level of a Cl^- ion dissolved in pure acetone lies only about 1 k.cal. higher than that of a Cl^- ion brought together with a CH_3Cl molecule within a medium of pure acetone. This difference which we have denoted by W will be of the same negligible magnitude for the other halogens.

The chief difference between the presentation in this paper, and that in the earlier paper of Ogg and Polanyi² lies in this small estimate of the electrostatic solvation terms compared with the large values attributed there. We have supposed that no resonance between CH_3X and X^- and $\text{X}^- \dots \overset{+}{\text{CH}_3} \dots \text{X}^-$ exists to produce a "smearing out" of the charge, and so the difference between the solvation energies of the transition state and of the reactant cannot be very large, since it can only arise from the interaction between the ion and the CH_3X molecule; this is the term which we have calculated roughly by the equation of Born.

Such resonances, which would lower the activation energy by stabilising the transition state, may well be of importance in other systems (see a forthcoming publication in *Nature* by M. G. Evans and Polanyi).

Department of Chemistry,
The University, Manchester.

GENERAL DISCUSSION

Dr. E. D. Hughes (London-Aberystwyth) said: In the verbal presentation of his paper, Baughan stated that the symmetrically-charged configuration, $\overset{+}{\text{Cl}} \dots \text{R} \dots \overset{-}{\text{Cl}}$, is unlikely to be a true representation of the transition state of the halogen-exchange reaction, because this would

lead to a much larger ionic-strength effect on the reaction rate than that which is actually observed. A consideration of the magnitude and distribution of the charges in the above formulation of the transition state, in relation to those in the reactants, shows, however, that a large ionic-strength effect is not to be expected on this basis,¹ and there is evidence that the effect is, in fact, appreciable.²

Mr. E. C. Baughan (*communicated*): In reply to Hughes:—

(1) The transition state $\overset{\frac{1}{2}}{\text{Cl}} \cdots \text{R} \cdots \overset{\frac{1}{2}}{\text{Cl}}$ would be an ion, of larger radius than Cl' . In very dilute solution, where the Debye-Hückel limiting law holds, there should therefore be no salt effect on either model. In the more concentrated solutions, for which all the experimental data available have been obtained, there would be a salt effect depending on the effect of ionic radius on the activity coefficient. For Hughes' model, this effect would be expected to be small and negative—by analogy with data for activity coefficients in water. Our model, in which the radius over which the charge is "smeared" is the same as that of the Cl' ion, should give practically zero salt effect. Unfortunately, a quantitative calculation is hardly possible, since so little is known about the theory of such stronger electrolyte solutions, and the only extant activity-coefficient data for acetone (as far as I am aware) are those of Robinson³ on iodide solutions below 0.004 N.

Although, therefore, this question could be answered by observations on salt effects, a definite answer can hardly be given in the present state of solution theory. A more powerful argument is this: The solvation energy E of a large ion is considerably less than that of a small one. The "smearing" out of charge from $\text{Cl}-\text{R} \cdots \text{Cl}'$ to $\overset{\frac{1}{2}}{\text{Cl}} \cdots \text{R} \cdots \overset{\frac{1}{2}}{\text{Cl}}$ would involve an increase in activation energy due to this change ΔE in solvation energy (*i.e.* the W term of our equation 7) would be increased from 1 k.cal. to ΔE ; various approximate estimates of this give values from about 15 k.cal. for the iodide reaction to 25 for the chloride). Unless, therefore, the resonance-energy of this smearing-out of charge is at least not less than ΔE , the "smearing-out" of charge is not energetically profitable. Such values for the resonance-energy seem improbably large, and the agreement of our calculated values with experiment would have to be explained (on Hughes' model) as due to a fortuitous equality of these resonance-energies with the appropriate ΔE 's.

(2) The experimental evidence is ambiguous. Bergmann, Polanyi, and Szabo⁴ found a considerable negative salt effect in the reaction $\text{RI} + \text{I}' \rightarrow \text{RI} + \text{I}'$ in acetone over the range 0.50–0.30 N. NaI ; the paper of Hughes, Juliusberger, Masterman, Topley and Weiss² confirms this for the two concentrations 0.10 N., and 0.16 N. The fact that I had in mind was that, in diluter solutions, Conant and Hussey⁵ found no observable salt effect in the reaction of benzyl chloride with iodide ion in 0.0134 N., 0.04 N. KI and 0.04 N., 0.08 N. NaI , which shows the salt effect to be small at concentrations still far too large for the Debye-Hückel limiting law to hold. The experimental position is further obscured, however, by the fact that the usual method of purifying acetone (that of Conant and Hussey),⁵ which was applied by all these authors, may easily leave 0.05 N. water.⁶ This concentration is of the same order as those of the ions, and this water would tend to be preferentially concentrated round them.

Dr. E. D. Hughes (*communicated*): Baughan and I now agree that, at the concentrations for which experimental data are available, the spread-

¹ Cf. *this vol.*, pp. 608, 617, and 665.

² Cf. Hughes, Juliusberger, Masterman, Topley and Weiss, *J.C.S.*, 1935, 1525.

³ *J. Physic. Chem.*, 1928, 32, 1089.

⁴ *Z. physik. Chem.*, B, 1933, 20, 161.

⁵ *J.A.C.S.*, 1935, 47, 483.

⁶ Cp. Lannung, *Z. physik. Chem.*, A, 1932, 161, 258.

in $\frac{1}{2}$ of the charge in the transition state model $\text{Cl}^{\frac{1}{2}-} \dots \text{R} \dots \text{Cl}^{\frac{1}{2}-}$ would probably lead to an appreciable negative salt effect, while the effect expected on the basis of the model used in the calculations of Baughan and Polanyi would be negligible. Concerning the experimental results summarised by Baughan (above), it should be stated that the polarimetric method used by Polanyi and by my colleagues and me is more amenable to accurate measurements than the method used by Conant and Hussey. And since the polarimetric experiments indicate that an appreciable salt effect does exist, the evidence to be derived from this source is, on the whole, favourable to my model. With regard to the calculated activation energies, there is, of course, some uncertainty in the calculation; and, owing to the sensitiveness of the energy to the stretching distance, deviations of 5 or even 10 k.cal. could probably be accommodated.⁷ The calculation of the effect of solvation is also highly uncertain. Differences, ΔE , in the solvation heats of the initial and the transition ions (distributed-charge model), of the order of magnitude of the figures mentioned by Baughan, may be expected for water as solvent, but not for acetone, to which the experimental data apply. While therefore appreciating the usefulness of the model adopted by Baughan and Polanyi as a basis for calculation, I am not convinced that the symmetrically-charged representation of the transition state can be discounted on the evidence presented.

Prof. C. K. Ingold (*London-Aberystwyth*) asked why it was that, since the main part of the energy was determined by the sizes of the extruded halogen as combined atom and as anion, and could be calculated without reference to the entering halogen, the method was confined to symmetrical substitutions.

Dr. R. P. Bell (*Oxford*) said: The reason that the method described by Baughan is limited in the first instance to symmetrical exchanges can be expressed as follows. In the symmetrical case the transfer of an electron without change of internuclear distance (*e.g.* $\text{Cl}-\text{R} \dots \text{Cl}^- \rightarrow \text{Cl}^-\dots\text{R}-\text{Cl}$) involves no change of energy for any symmetrical configuration, and the activation energy is thus found simply by determining the symmetrical configuration which can be produced most economically from the energy point of view. In an unsymmetrical exchange such as $\text{Cl}-\text{R} \dots \text{I}^- \rightarrow \text{Cl}^-\dots\text{R}-\text{I}$ there will be only one (unsymmetrical) configuration for which the electron transfer can take place without energy change, and in order to find this configuration the variation of both the internuclear distances must be considered separately. In other words, the symmetrical case can be treated by means of energy curves, while the unsymmetrical case demands the consideration of energy surfaces. Hence although the calculations of Baughan and Polanyi should give activation energies of the right order of magnitude for the unsymmetrical exchanges commonly observed they may fail in points of detail such as the effect of replacing one halogen by another.

Prof. M. Polanyi and Mr. Baughan in reply (*communicated*): We are in substantial agreement with Bell's comments, and hope to be able to extend our theoretical approach to cover the unsymmetrical cases by considering these repulsive forces. A first approximation would predict that the rate of the reaction $\text{I}' + \text{RCl} \rightarrow \text{RI} + \text{Cl}'$ should be intermediate between those of the two symmetrical cases $\text{RCl} + \text{Cl}'$, $\text{RI} + \text{I}'$. The only available data (those of Szabo on the racemisation of *d*- $\text{C}_4\text{H}_9\text{CH}_2\text{CHhal}$ by halide ions quoted by Ogg and Polanyi⁸ agree with this view, the activation energies being respectively 21.8 ($\text{I}' + \text{RCl}$), 23.7 ($\text{Cl}' + \text{RCl}$), and 17.4 ($\text{I}' + \text{RI}$) K.cal.

⁷Cf. Baughan and Polanyi's paper.

⁸*Trans. Faraday Soc.*, 1935, 31, 616.

THE MECHANISM AND KINETICS OF ELIMINATION REACTIONS.

By E. D. HUGHES AND C. K. INGOLD.

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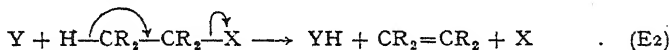
Arrangement.

- (1) Duality of Mechanism.
 - (1.1) The Bimolecular Mechanism.
 - (1.2) The Unimolecular Mechanism.
- (2) Environmental Influences.
 - (2.1) Concentration of the Reagent.
 - (2.2) Basicity of the Reagent.
 - (2.3) Ionising power of the Medium.
 - (2.4) Temperature.
- (3) Constitutional Influences.
 - (3.1) Hofmann's Rule and the General Inductive Effect.
 - (3.2) Saytzeff's Rule and the Tautomeric Effect.
 - (3.3) Co-existence of the General Inductive and Tautomeric Effects.

(1) Duality of Mechanism.

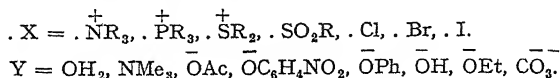
Substitution and elimination occur together so often as to suggest that the duality of mechanism, which has been established for substitution and has proved the key to its interpretation, might have some parallel in the mechanism of elimination. We shall show that, in fact, a quite similar duality is general for elimination, and that its recognition permits substantial progress in the interpretation of environmental and structural influences on this reaction.

(1.1) The Bimolecular Mechanism.—In this process, which was established as a general mechanism of elimination by Hanhart and Ingold in 1927, a reagent possessing basic properties extracts the protonic part of a combined hydrogen atom, whilst an electron-attracting group simultaneously separates in possession of an extra electron. It is necessary that the hydrogen atom and the electron attractor shall be bound to adjacent carbon atoms in the original molecule in order that the atomic electron shells shall remain complete throughout the change. Two bonds are thus broken, but each fission assists the other, the two together constituting a single synchronised act. In the equation

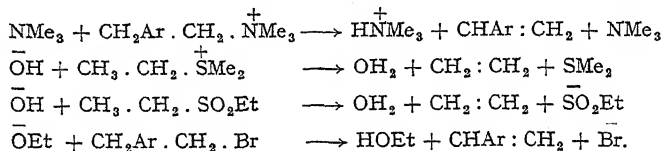


arrows have been introduced to show the direction of the electron transfers, but we have placed no sign-labels on X and Y because there are various possibilities. Originally the basic reagent Y may be either neutral or negatively charged, and the electron-attracting group X may independently be either positive or formally neutral: all that the nature of the reaction necessitates is that, after the change, the formal charge of Y will be more positive by one unit, and that of X more negative by one unit, than before.

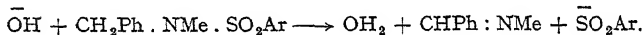
This mechanism is described as "bimolecular" and distinguished by the label E2. Its consequences have previously been illustrated with respect to the formation of olefins from tetra-alkylammonium salts,¹ certain specially chosen tetra-alkylphosphonium salts,² trialkylsulphonium salts,³ dialkyl and alkyl aryl sulphones⁴ and alkyl halides.⁵ Neutral or negatively charged reagents, varying in basicity from water to alkoxide ions, have been employed:



The following reactions are typical of those investigated in this connection:

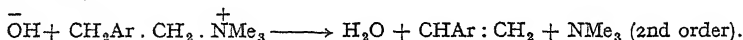


An example of the formation, by the same mechanism, of an azomethine in place of an olefin is provided by the "anomalous hydrolysis," by means of alkali, of a sulphonamide to a sulphinic acid.⁶



Eliminations proceeding by the bimolecular mechanism normally exhibit second order kinetics. This has been formally established for

$Y = \text{OH}^-$ and OEt^- in the case of ammonium, sulphonium, and halogen compounds, $X = \cdot \overset{+}{\text{N}}\text{R}_3, \cdot \overset{+}{\text{S}}\text{R}_2, \cdot \text{Hal}$.⁷ The following is an example ($\text{Ar} = \text{Ph}$):



However, just as with substitutions, so also with eliminations, a bimolecular mechanism is not necessarily associated with second order kinetics. In the preceding example, a strongly basic reagent is employed;

¹ Hanhart and Ingold, *J. Chem. Soc.*, 1927, 997; Ingold and Vass, *ibid.*, 1928, 3125; v. Braun, Teuffert and Weissbach, *Annalen*, 1929, 472, 121; v. Braun and Buchman, *Ber.*, 1931, 64, 2610; v. Braun and Hamann, *Ber.*, 1932, 65, 1580; Ingold and Patel, *J. Chem. Soc.*, 1933, 68; Hughes and Ingold, *ibid.*, p. 523; Hughes, Ingold and Patel, *ibid.*, p. 526.

² Fenton and Ingold, *ibid.*, 1929, 2342; Hey and Ingold, *ibid.*, 1933, 531.

³ v. Braun, Teuffert and Weissbach, *loc. cit.*¹; Ingold, Jessop, Kuriyan and Mandour, *J. Chem. Soc.*, 1933, 533; Ingold and Kuriyan, *ibid.*, p. 991; Hughes and Ingold, *ibid.*, p. 1571; Gleave, Hughes and Ingold, *ibid.*, 1935, 236.

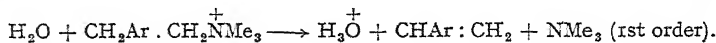
⁴ Fenton and Ingold, *ibid.*, 1928, 3127, *ibid.*, 1929, 2338; *ibid.*, 1930, 705.

⁵ Olivier, *Rec. trav. chim.*, 1934, 53, 1093; Hughes, *J. Amer. Chem. Soc.*, 1935, 57, 708; Hughes and Ingold, *J. Chem. Soc.*, 1935, 244; Hughes, Ingold and Shapiro, *ibid.*, 1936, 225; Hughes and Shapiro, *ibid.*, 1937, 1177; *idem*, *ibid.*, p. 1192; Hughes, Ingold, Masterman and MacNulty, *ibid.*, 1940, 899.

⁶ Holmes and Ingold, *ibid.*, 1926, 1305.

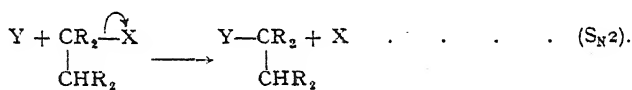
⁷ Green and Sutherland, *ibid.*, 1911, 99, 1174; Hughes and Ingold, *ibid.*, 1933, 523; *ibid.*, p. 1571; Gleave, Hughes and Ingold, *loc. cit.*³; Hughes, Ingold and Shapiro, *loc. cit.*⁵; Hughes and Shapiro, *loc. cit.*⁵; Hughes, Ingold, Masterman and MacNulty, *loc. cit.*⁵; unpublished researches by M. L. Dhar, F. R. Webb and L. I. Woolf.

but, if the hydrogen atom of the organic molecule is made more vulnerable by an appropriate constitutional change, a weaker base will suffice, —for instance, a solvent molecule. After introducing a para-nitro-group into the ammonium cation, the following reaction was observed,⁸ which proved to be of first order in aqueous solution ($\text{Ar} = \text{C}_6\text{H}_4\text{NO}_2\text{-}p$):



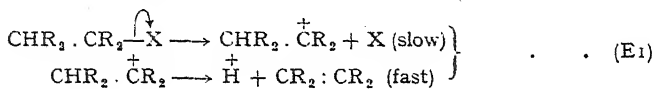
(It is to be noted that an instantaneous proton transfer from the formed H_3O^+ to the NMe_3 removes the latter immediately it is produced, and thus prevents kinetic complications due to the incursion into the elimination process of NMe_3 as an additional basic reagent.) In spite of its kinetic order, the above reaction almost certainly pursues the bimolecular mechanism, as is indicated, for instance, by the large increases of speed which are observed when small amounts of some stronger base than water are added initially.

Many of the conditions which favour elimination by the bimolecular mechanism (E_2) are similar to those which promote nucleophilic substitution by the bimolecular mechanism ($\text{S}_\text{N}2$). Thus, the latter reaction often accompanies the former. Writing the substitution process for comparison, we notice that the electron transfer takes the direction from Y to X just as before, but now operates through a shorter system:



Naturally, the electrical charges of X and Y have the same latitude and limitations as before.

(1.2) The Unimolecular Mechanism.—In this process, first indicated as a general mechanism by Hughes in 1935, an electron attracting group X separates with an additional electron, leaving a carbonium ion which subsequently loses a proton to the solvent or some other proton acceptor. The reaction thus has two stages, of which the first, the heterolytic fission⁹ of the bond C—X , is regarded as rate-determining. Accordingly the rate is independent of any added base (unless this is present in a sufficiently concentrated form to produce a salt or solvent effect on the initial bond fission). Naturally, the electron attracting group X may be formally neutral or positively charged before the reaction, becoming, as the case may be, negatively charged or neutral afterwards:



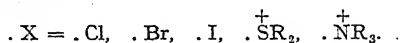
This mechanism is named “unimolecular,” and is distinguished by the label E_1 . It was first established for halogen compounds,¹⁰ and

⁸ Hughes and Ingold, *J. Chem. Soc.*, 1933, 523.

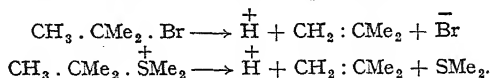
⁹ The terms “homolysis” and “heterolysis” connote bond fission according to the schemes $\text{A} \cdot \cdot \text{B}$ and $\text{A} \cdot \cdot \cdot \text{B}$ respectively (the dots represent electrons) independently of the charges carried by the atoms and of any concomitant covalency changes (*Trans. Faraday Soc.*, 1938, 34, 227).

¹⁰ Hughes, *loc. cit.*⁸; Hughes, Ingold and Scott, *Nature*, 1936, 138, 120; *J. Chem. Soc.*, 1937, 1271; Hughes, Ingold and Shapiro, *ibid.*, p. 1277; Cooper, Hughes and Ingold, *ibid.*, p. 1280; Hughes and MacNulty, *ibid.*, p. 1283.

later for sulphonium salts; ¹¹ unfinished experiments suggest that it is important for ammonium salts also:

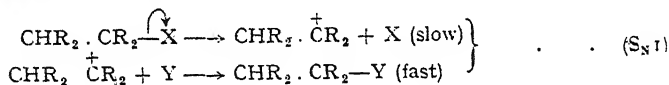


The following decompositions in aqueous solvents are typical of eliminations in which this mechanism is prominent:



Eliminations taking place by the unimolecular mechanism normally exhibit first order kinetics. This has been formally established for alkyl chlorides and bromides,¹² and for sulphonium salts.¹¹ Deviations from first order kinetics due to salt effects, and to the reversibility of the rate-determining stage of mechanism E1, have been indicated in the case of alkyl halides.¹³

Many of the conditions which promote unimolecular elimination (E1) also favour unimolecular substitution (S_NI), and thus the former process is commonly accompanied by the latter:



It has often been pointed out in relation to substitution that the bimolecular and unimolecular mechanisms must merge into each other: in those cases in which the observations can be described in terms of a concurrence of the processes S_N2 and S_NI, we actually envisage intermediate mechanisms, rather than a superposition of the extremes. An entirely similar merging of mechanisms is assumed for elimination: in mechanism E2 the attack of Y assists the separation of X, whilst in the E1 mechanism Y gives no such aid; there must, however, be *degrees* of assistance which X might require, and a suitably situated Y could render.

The two unimolecular mechanisms S_NI and E1 have a common slow stage, and our views on unimolecular elimination will therefore take account of the information regarding the carbonium ion, which has been derived from stereochemical¹⁴ and detailed kinetic¹⁵ studies of unimolecular substitution. We know that no intervention by any specific reagent is required before, as a minimum, the C—X bond fission has passed beyond the transition state, which theory shows to occur at an extension of rather more than 0.5 Å in excess of the normal bond length. It is clear, nevertheless, that the fate of the less stable carbonium ions may be determined whilst the receding X is still only a few atomic diameters away. On the other hand, the more stable carbonium ions may attain equilibrium dissociation, and in this case we have strong evidence that much of their stability is derived from a complex solvation shell.

¹¹ Unpublished investigations by K. A. Cooper, B. J. MacNulty and L. I. Woolf.

¹² Hughes, Ingold and Shapiro, *J. Chem. Soc.*, 1937, 1277; Cooper, Hughes and Ingold, *loc. cit.*¹⁰; Hughes and MacNulty, *loc. cit.*¹⁰; unpublished investigation by M. L. Dhar.

¹³ Bateman, Hughes and Ingold, *J. Chem. Soc.*, 1940, 960.

¹⁴ Cowdrey, Hughes, Ingold, Masterman and Scott, *ibid.*, 1937, 1252.

¹⁵ Bateman, Church, Hughes, Ingold and Taher, *ibid.*, 1940, 979.

The identity of the rate-controlling steps of mechanisms S_N1 and $E1$ suggests a comparison which should serve to confirm the kinetic evidence of the nature of these mechanisms. Both assume the slow formation of the carbonium ion; the rapid stages of the two mechanisms differ, but both are reactions of the carbonium ion from which the group X has been removed. Therefore if we operate with a series of compounds RX' , RX'' , . . . , containing the same R but a variable X, the specific rate of the total unimolecular reaction,

$$k_{\text{heterolysis}} = k_1 = k_{S_N1} + k_{E1},$$

might vary quite largely, but the proportion, k_{E1}/k_1 , in which the carbonium ion will decompose in a particular direction should be independent of the nature of X. Actually this is a simplifying over-statement; for, inasmuch as X may not be far away when the fate of $\overset{+}{R}$ is determined, X could have some influence on the relative speeds of the alternative decompositions of $\overset{+}{R}$. However, this effect would be expected to lead only to minor variations in the ratio, k_{E1}/k_1 , and should certainly not change its order of magnitude; whereas a suitable variation of X might change even the order of magnitude of the rates, k_1 , k_{E1} , and k_{S_N1} , themselves. Some examples, in which X may be Cl, Br, I, $\overset{+}{S}Me_2$ are indicated in Table I. The comparisons show that whilst k_1 may be changed by factors of more than 100, the corresponding variation of k_{E1}/k_1 is represented by factors of not more than 1.3.

TABLE I.—EFFECT OF VARIATION OF X ON THE TOTAL RATE CONSTANT k_1 (SEC.⁻¹) AND ON THE RATE RATIO k_{E1}/k_1 IN THE UNIMOLECULAR DECOMPOSITIONS OF RX.

Solvent.*	Temp.	R.	X.	$10^6 k_1$	k_{E1}/k_1
" 60 % aq. EtOH "	100.0°	β -n-Octyl	{ Cl	0.805	0.13
			{ Br	26.8	0.14
" 50 % aq. EtOH "	25.0°	<i>tert.</i> -Butyl	{ Cl	0.854	0.168
			{ Br	37.2	0.126
			{ I	90.1	0.129
" "	65.3°	" "	{ Cl	89.7	0.363
			{ $\overset{+}{S}Me_2$	11.8	0.357
" "	25.2°	<i>tert.</i> -Amyl	{ Cl	1.50	0.333
			{ Br	58.3	0.262
			{ I	174	0.260
" "	50.0°	" "	{ Cl	28.5	0.403
			{ $\overset{+}{S}Me_2$	6.66	0.478

[* " x % aq. EtOH " means a mixture of x vol. of ethyl alcohol with (100-x) vol. of water.]

(2) Environmental Influences.

It has been explained that when an alkyl halide or alkyl 'onium salt is decomposed in solution in such a way as to produce an olefin, we

normally observe two kinetically distinguished reactions, each of which is duplex. There is a second order reaction, which consists of the simultaneous and independent reactions, substitution and elimination (S_N2 and $E2$) in certain proportions; and superposed on these a first order reaction is found, which also consists of simultaneous substitution and elimination (S_N1 and $E1$), but in different proportions.

The relative importance of these competing processes will naturally depend on the substances involved and on the conditions. In attempting a description and explanation, it is convenient to distinguish the following influencing factors :

1. The concentration of the reagent.
2. The basicity of the reagent.
3. The ionising power of the medium.
4. The temperature.
5. The structure of the alkyl derivative.

The first four of these factors may be grouped together as "environmental": they are to be dealt with in the immediately following subsections. The last factor deserves extended treatment, and will be discussed in section 3.

Before proceeding to details, it will be convenient to set down a summary of the ways in which the environmental factors have been found qualitatively to influence (i) the total bimolecular reaction relatively to the total reaction, (ii) the bimolecular olefin production relatively to the total bimolecular reaction, and (iii) unimolecular olefin production relatively to the total unimolecular reaction,—three ratios which define the possible relative variation of the four simultaneous reactions. This is done in Table II, the entries in which hold good for both alkyl halides and alkyl 'onium salts, subject to the limitations indicated. We do not similarly summarise observed environmental effects on the absolute rates of the component reactions as these are not always the same for halides and 'onium salts.

TABLE II.—OBSERVED QUALITATIVE EFFECTS ON RATIOS OF SIMULTANEOUS REACTIONS.

Effect on— of increasing:	(i) $\frac{S_N2 + E2}{S_N2 + E2 + S_N1 + E1}$	(ii) $\frac{E2}{S_N2 + E2}$	(iii) $\frac{E1}{S_N1 + E1}$
(1) the concentration of the reagent . .	Increase	None	None.
(2) the basicity of the reagent . . .	Increase	Increase	None.
(3) the ionising power of the medium . .	Decrease	Decrease *	Decrease.
(4) the temperature .	Small *	Increase *	Increase.

[* Established only for alkyl halides.]

(2.1) Concentration of the Reagent.—Let us imagine a solvent, such as water, which is sufficiently ionising freely to allow unimolecular processes, and a reagent, such as hydroxide ion, nucleophilic enough readily to engage in bimolecular reactions. Then at low *pH* first order reactions will evidently dominate; and they will be characterised by the formation of olefin in a proportion which is constant, since it is given by

the ratio $E1/(S_N1 + E1)$ of the rates of reactions in which the hydroxide ion takes no part. This assumes that, in the fast stages of reactions S_N1 and $E1$, the carbonium ion is decomposed by a solvent molecule, without the intervention of the anion; and there is every indication that this is true in the hitherto investigated cases of unimolecular olefin formation. On the other hand, at very high pH the alkali-accelerated second order reactions will dominate; and they will produce a proportion of olefin which, although different, is likewise constant, because it is given by the ratio $E2/(S_N2 + E2)$ of reaction rates into which the alkali concentration enters identically. Between these extremes there must be a region of changing reaction order, and a correspondingly changing olefin proportion. Plotting the olefin proportion against the pH , we may expect to obtain a sigmoid curve like one of those shown in Fig. 1. In sub-section 2.2 we shall find that such curves rise steeply with powerful reagents such as hydroxide ions, although the slope is in general dependent on the basicity of the reagent.

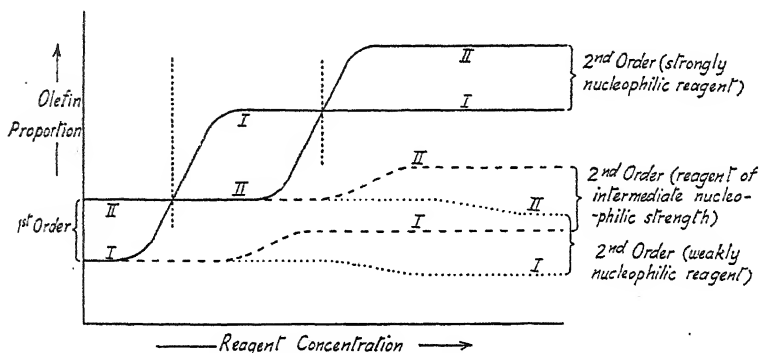


FIG. 1.—Schematic representation of the connection between proportion of olefin and concentration and basicity of reagent.

The importance of reaction order in relation to environmental effects, in particular, the effect of concentration, may be illustrated by reference to the controversy as to whether secondary alkyl halides yield larger proportions of olefins than tertiary or *vice versa*. An omission to consider kinetic phenomena has produced unjust criticisms of the opposing results of earlier investigators, but it is a fact that either relation between secondary and tertiary halides may be obtained according to conditions. The condition we are discussing in this sub-section is reagent concentration. Now it will be shown in section 3 that the extra α -alkyl branch present in a tertiary as compared with a secondary alkyl group must increase the proportion of olefin alike in the first order and in the second order reaction. But we know that the extra α -alkyl branch also promotes the ionisation of the tertiary halide; so that, on increasing the concentration of the basic reagent, the first order reaction will continue to dominate up to a larger concentration of reagent for the tertiary than for the secondary compound. Thus, for a reagent, such as hydroxide or ethoxide ion, which in second order reactions produces considerably more olefin than is given by either halide in its first order decompositions, the sigmoid curves for the secondary and tertiary alkyl compounds will intersect in two places, as illustrated by the full-line curves of Fig. 1. Curve I might represent a secondary and curve II a tertiary alkyl halide.

In the region of first order kinetics (left) the sequence is evidently *tert.* > *sec.*; in the mixed order region (middle) it is *sec.* > *tert.*; whilst in the second order region (right) it reverts to *tert.* > *sec.* The comparison of older results is complicated by the simultaneous variation of other factors, reagent basicity and solvent ionising power, the discussion of which does not belong to this sub-section, and we therefore illustrate in Table III the differences deduced above by means of data taken from a recent investigation¹⁶ of the alcoholysis of *isopropyl* and *tert.*-butyl bromides.

TABLE III.—TYPICAL PERCENTAGES OF OLEFIN PRODUCED IN ALCOHOLYSIS OF *ISO*-PROPYL AND *TERN*.-BUTYL BROMIDES IN NEUTRAL, DILUTE ALKALINE AND STRONGLY ALKALINE SOLUTION IN DRY ETHYL ALCOHOL AT 55°.

[NaOEt]	0.00	0.05	2.0
Reaction order	first	mixed	second
% Olefin { <i>iso</i> -PrBr	3*	71	79
<i>tert.</i> -BuBr	28	34	93
Sequence	<i>tert.</i> > <i>sec.</i>	<i>sec.</i> > <i>tert.</i>	<i>tert.</i> > <i>sec.</i>

[* Estimated from experiments under other conditions.]

(2.2) **Basicity of the Reagent.**—Both the second order reactions depend on the nucleophilic power of the reagent, because in both cases the attack is on an atomic kernel. Although it will never be possible to give a generally applicable quantitative value to nucleophilic power, it may be agreed that a fairly reliable qualitative index of this property of reagents is furnished by their basic strengths, as measured under arbitrary but definite conditions. Affinity for a proton is certainly a rough guide to affinity for other incompletely screened atomic kernels; and thus we cannot doubt that, corresponding to the increase of basic strength, nucleophilic power in general will increase along such a series as



The main effect of increasing the nucleophilic power of the reagent at constant concentration is to increase the rate of the total second order reaction both absolutely and relatively to the first order reaction: the ratio $(S_N2 + E2)/(S_N2 + E2 + S_N1 + E1)$ must increase. An illustration has been given with respect to trialkylsulphonium salts: thus, at concentrations at which the bromide ion would not participate in a detectable second order reaction with sulphonium cations, the phenoxide ion superposed a fairly rapid, and the hydroxide ion a very rapid, second order reaction on the first order background process.¹⁷

In second order substitution the attack of the reagent is on carbon, whilst in second order elimination it is on hydrogen. Therefore, the olefin proportion, $E2/(S_N2 + E2)$, in second order decomposition, must depend on the relative nucleophilic activities of the reagent towards hydrogen and towards carbon. As already noted, the parallelism between these properties is by no means exact; and the general direction of the deviation is that whilst strong bases are strongly nucleophilic towards carbon, weaker bases retain a more than proportional activity towards carbon. An extreme example is that of the bromide ion, which has hardly any nucleophilic activity for hydrogen (basicity), but retains

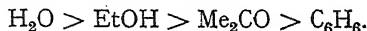
¹⁶ Hughes, Ingold, Masterman and MacNulty, *loc. cit.*⁵; unpublished measurements by M. L. Dhar.

¹⁷ Cleave, Hughes and Ingold, *loc. cit.*³

a moderate activity for carbon, as is shown, for instance, by the considerable velocity of halogen-exchange reactions between halide ions and alkyl halides. Thus, as we pass from the hydroxide ion to the phenoxide ion, the acetate ion and other anions of weak or moderately strong acids, we must observe a decrease in the bimolecular olefin proportion. Such a decrease is the general experience, and this is why organic chemists, desiring to convert a halogen compound into an alcohol with a minimum of olefin production, frequently prefer to operate with potassium acetate and to saponify the resulting ester, rather than to treat the halide with hydroxide ions directly.

The effect of this decreased bimolecular olefin production on the relation between the reagent concentration and the total proportion of olefin is illustrated by the chain and dotted curves of Fig. 1; they are supposed to apply to successively less basic reagents than that of the full-line curves. In each of the three cases, curves I and II are drawn to represent a constitutional difference, such as that between a secondary and a tertiary alkyl compound, determining that, so long as reactions of the same kinetic order are compared, the compound of curve II will produce the greater proportion of olefin. It will be observed that the intersections of the full-line curves do not arise with the chain or dotted curves, so that the effect of the constitutional difference remains in the same direction throughout the concentration range. Thus we can explain how it comes about that, although in reactions involving hydroxide or ethoxide ions secondary and tertiary halides may, according to the conditions, stand in either order with respect to the proportions in which they yield olefin (preceding sub-section), no such ambiguity has been observed in reactions with phenoxide or acetate ions, for which tertiary halides yield the larger proportion of olefin under all conditions investigated.¹⁸

(2.3) Ionising Power of the Medium.—The illustrations to be given in this sub-section will not require us to attempt the difficult task of constructing a precise definition of ionising power in relation to the reactions under consideration. It will suffice to take the usual crude, but simple, view: an ionising solvent is one which solvates charged centres with liberation of energy; because of its intense local field, water does this *par excellence*; and it is followed, in order of diminishing effectiveness, by the simpler alcohols, non-protonic dipolar solvents, and non-dipolar solvents; *e.g.*,



The argument we shall use in order to deduce the effect of solvent changes on olefin elimination is the same as that previously applied by us to nucleophilic substitution.¹⁹ The effect of solvation on the rate of each activated process is assumed to arise from the difference between the solvation energy of the activated (or "transition") state and that of the initial state. The following postulates are necessary concerning the degree of solvation to be expected from the presence of electric charges: (i) solvation will increase with the magnitude of the charge; (ii) solvation will decrease with increasing distribution of a given charge; (iii) the decrease of solvation due to distribution will be less than the decrease due to destruction of the same amount of charge. By applying

¹⁸ Segaller, *Chem. Soc.*, 1913, 103, 1430; Mereshkowsky, *Annalen*, 1923, 431, 231.

¹⁹ Hughes and Ingold, *J. Chem. Soc.*, 1935, 252.

these rules to the initial and transition states, we can deduce the effect of solvation on the energy of activation and the rate. The direction of the effect being thus determined, we know that its magnitude will be greater the more ionising the solvent.

The application of these arguments to the second order reactions S_N2 and $E2$, and to the common slow stage which determines the sum of the rates of the first order processes, $S_N1 + E1$, is indicated in Table IV. The cases represented include alkyl halides and 'onium salts, but do not, of course, exhaust the categories of reactants which can produce simultaneous substitution and elimination. The adjectives in the last column have purely relative significance, and result from the application of postulate (iii).

TABLE IV.—PREDICTED MEDIUM EFFECTS ON RATES OF COMPETING REACTIONS

Process.	Disposition of Charges.		Effect of Activation on Charges.	Effect on Rate of Ionising Media.
	Initial State.	Activated State.		
[Example : Attack of Anions on Alkyl Halides.]				
$k_2 \left\{ \begin{array}{l} S_N2 \\ E2 \end{array} \right.$	$\bar{Y} + RX$	$\left. \begin{array}{c} \delta^- \dots R \dots \delta^- \\ \bar{Y} \dots H \dots C \dots C \dots X \\ \delta^- \dots \delta^- \\ R \dots X \end{array} \right\}$	Dispersed	Small decrease.
$k_1 = S_N I + E I$	RX	$\left. \begin{array}{c} \delta^+ \dots \delta^- \\ R \dots X \end{array} \right\}$	Increased	Large increase.
[Example : Decomposition of 'Onium Salts.]				
$k_2 \left\{ \begin{array}{l} S_N2 \\ E2 \end{array} \right.$	$\bar{Y} + R\overset{+}{X}$	$\left. \begin{array}{c} \delta^- \dots R \dots \delta^+ \\ \bar{Y} \dots H \dots C \dots C \dots \delta^+ \\ \delta^- \dots \delta^+ \\ R \dots X \end{array} \right\}$	Reduced	Large decrease.
$k_1 = S_N I + E I$	$R\overset{+}{X}$	$\left. \begin{array}{c} \delta^+ \dots \delta^+ \\ R \dots X \end{array} \right\}$	Dispersed	Small decrease.

It will be evident that, for both alkyl halides and alkyl 'onium salts, the effect of increasing the ionising power of the solvent is to increase the relative importance of the first order reaction. But the reason is different in the two cases: with alkyl halides the main cause is the increased rate of the first order processes, whilst with 'onium salts it is the decreased speed of the second order reactions. A large mass of data is available to illustrate these generalisations: we have collected in Table V a few values relating to alcohol-water mixtures. In the last column the run of the figures is summarised in qualitative terms for comparison with the predictions of Table IV.

On examining the top two lines of Table IV, one observes a difference in the dispersal of charge in the activated states of the two bimolecular reactions of alkyl halides: the dispersal is greater for the elimination process, as the transition state of this reaction provides more atoms over which the unit negative charge may be distributed. Therefore ionising media must suppress reaction $E2$ more than they suppress reaction S_N2 ; accordingly they must diminish the bimolecular olefin ratio $E2/(S_N2 + E2)$. This argument does not apply to the second order reactions of 'onium salts, since the two activated complexes are here formed with reductions of charge, which theory does not enable us

to compare. It can, however, be applied to the rapid steps of the two unimolecular reactions, that is, to the alternative decompositions of the carbonium ion, no matter whether this is derived from halides or from 'onium salts. We here assume what has never been completely proved, namely, that these fast solvolytic reactions are activated processes.²⁰

TABLE V.*—EXAMPLES OF OBSERVED MEDIUM EFFECTS ON THE REACTION RATES.

	Vol. % H ₂ O in aqueous EtOH				Qualitative Description.
	0	20	40	50	
Alkyl Halides.					
$10^4 k_2$ for Pr β Br at 55° (a)	2.05	1.20	0.875	—	Small decrease.
$10^6 k_1$ for Bu γ Cl at 25° (b)	1.71	9.15	126	367	Large increase.
Alkyl 'Onium Ions.					
$10^3 k_2$ for MeSMe $_2^+$ at 100° (c)	742	17.8	1.51	—	Large decrease.
$10^4 k_1$ for Am γ SMe $_2^+$ at 65.3° (d)	—	5.99	—	4.54	Small decrease.

[* Time units, seconds. (a) Hughes, Ingold and Shapiro, *loc. cit.*⁵; Hughes, Ingold, Masterman and MacNulty, *loc. cit.*⁵; (b) Hughes, *J. Chem. Soc.*, 1935, 256; cf. Cooper, Hughes and Ingold, *loc. cit.*¹⁰; (c) Gleave, Hughes and Ingold, *loc. cit.*³; (d) $\text{Am}^n = \text{tert.}-\text{Amyl}$; unpublished experiments by B. J. MacNulty.]

The activated states again involve charge dispersal, which is more extensive for the elimination reaction. Hence, for both halides and 'onium salts, ionising solvents must reduce the unimolecular olefin ratio, $\text{EI}/(\text{S}_\text{N}\text{I} + \text{EI})$.

In illustration of these predictions of theory, some figures relating to alcohol-water mixtures have been assembled in Table VI. They

TABLE VI.*—TYPICAL MEDIUM EFFECTS IN OLEFIN PROPORTIONS IN KINETICALLY UNIFORM REACTIONS.

	Vol. % H ₂ O in aqueous EtOH.			
	0	20	40	50
$\frac{100\text{E}_2}{\text{S}_\text{N}2 + \text{E}_2}$ for $\text{Pr}\beta\text{Br}$ at 55° (a)	79.0	58.6	54.9	—
$\frac{100\text{EI}}{\text{S}_\text{N}\text{I} + \text{EI}}$ { for Am^nBr at 25° (b)	36.3	26.2	20.2	—
for $\text{Am}^n\text{SMe}_2^+$ at 50° (c)	—	47.8	—	36.3

* (a) As a of Table V; (b) $\text{Am}^n = \text{tert.}-\text{amyl}$; Hughes and MacNulty, *loc. cit.*¹⁰; unpublished experiments by M. L. Dhar; (c) Unpublished experiments by B. J. MacNulty.]

²⁰ It has been proved that the reactions of carbonium ions with added anions are activated (Bateman, Church, Hughes, Ingold and Taher, *J. Chem. Soc.*, 1940, 1007), and we shall show later that this is true also for the proton-transfer reactions of carbonium ions with neutral solvent molecules (fast stage of E_1), but there is as yet no evidence concerning the associative reaction of carbonium ions with solvent molecules (fast stage of $\text{S}_\text{N}\text{I}$).

refer to the percentages of olefin produced in the kinetically isolated second order decomposition of an alkyl halide, or in the first order decomposition of either a halide or an 'onium salt. In all cases the proportion is smaller in the more aqueous solvent.

The effect of change of medium is not only to alter the proportion in which olefin is produced in reactions of uniform order, but also, as we have already seen, to alter the relative importance of the first and second order reactions, and thereby once again to alter the proportion of olefin. The combined result of these effects, in the case of alkyl halides, is represented schematically in Fig. 2, in which the reagent concentration is supposed to be kept constant, and the solvent made progressively more ionising from left to right. The full-line curves relate to a strongly basic reagent, such as hydroxide ion, which will produce much more olefin in second order reaction than the alkyl halide yields in its first order decomposition. The proportion of olefin should then fall with increasing ionising power of the medium, as shown by

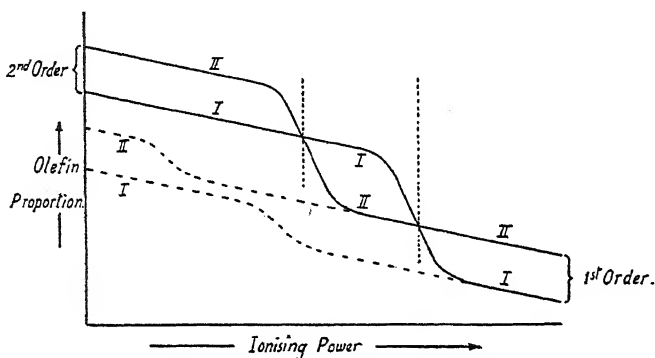


FIG. 2.—Schematic representation of the connection between proportion of olefin and ionising power of solvent.

these curves, the steep parts of which correspond to the changes of reaction order.

The two curves, I and II, are drawn to show the way in which solvent influences may reverse the effect to be expected from a constitutional difference, such as that between a secondary and a tertiary alkyl halide. As the ionising power of the solvent is increased, the first reaction to change from the second to the first kinetic order will be that of the tertiary halide (curve II), which in both second and first order reactions furnishes more olefin than the secondary compound (curve I). The olefin yields in second order reactions with a strongly basic reagent being considerably greater than in first order decompositions, the curves will have two intersections. Thus, the sequence *tert.* > *sec.*, applying to both the second and first order regions of the diagram, becomes reversed to *sec.* > *tert.* in the central section in which both kinetic orders are present. This is one of the causes of the apparent inconsistency of early results relating to the relative yields of olefin from secondary and tertiary alkyl halides. Thus Nef,²¹ using dry alcoholic alkali, found the sequence *tert.* > *sec.*, whilst Brussoff,²² with aqueous alcoholic alkali,

²¹ Nef, *Annalen*, 1899, 309, 126; 1901, 318, 1.

²² Brussoff, *Z. physikal. Chem.*, 1900, 34, 129.

obtained *sec.* > *tert.* When much less basic reagents are employed the bimolecular olefin production is much smaller, and the intersections may then disappear (broken curves) with results similar to those illustrated earlier in a corresponding connection. The general slope of the full-line curves explains the traditional use of dry alcoholic rather than aqueous alkali in preparative organic chemistry when the desired product is an olefin.

Logically we ought to include a discussion of neutral salt effects in this section, for the theory corresponds closely to that already given for solvent changes. Just as their effect depends on the energy of attraction of dipole molecules for electric charges that become modified in activation, so salt effects depend on the attraction of ions for the same charges; indeed, it may be said that one way of making a solvent more ionising is to dissolve ions in it. However, detailed discussion is omitted, since the experimental study of salt effects in substitution has not yet been extended to elimination.

(2.4) Temperature.—Observations with regard to the effect of temperature on the bimolecular reactions undergone in aqueous solvents by alkyl halides in conditions leading to olefin elimination may be summarised as follows. The second order substitution and elimination reactions of primary and secondary alkyl chlorides, bromides and iodides all have temperature coefficients corresponding to apparent (Arrhenius) energies of activation lying within the range 23 ± 2 kilocal./g.-mol. But, for any given pair of simultaneous second order processes, the elimination has, in all the cases studied, been found to possess an apparent activation energy higher by 1.2 kilocal./g.-mol. than that of the substitution. The elimination thus has the larger temperature coefficient, so that a rise of temperature increases the proportion in which olefin is formed. The temperature coefficient of the second order reactions of 'onium salts are of the same order of magnitude, but the measurements are not yet sufficiently numerous to justify generalisations.

With regard to first order processes, the temperature coefficients of the total first order reaction, that is, of the rate-determining ionisation, of secondary and tertiary alkyl chlorides, bromides and iodides, are once again rather closely grouped, and correspond to apparent activation energies which lie mostly within the range 22 ± 2 kilocal./g.-mol. For alkylsulphonium ions the grouping is also close, but the values strikingly larger, namely, 32 ± 1 kilocal./g.-mol.²³

As to the fast stages of the separate first order processes, namely, those decompositions of the pre-formed carbonium ion which lead, on the one hand, to a substitution product, and on the other to elimination, we naturally do not know the separate temperature coefficients; but we do know that they differ in such a way that, once more, a rise of temperature increases the proportion in which olefin is produced. The increases are such as would correspond to apparent activation energies which are larger by about 2.5 kilocal./g.-ion for the elimination than for the substitution.²⁴

In order to illustrate these points a selection of figures relating to

²³ In non-aqueous solvents the range is wider, but the centre of gravity of the values is the same: 32 ± 4 kilocal./g.mol. (v. Halban, *Z. physikal. Chem.*, 1909, **67**, 129; Essex and Gelormini, *J. Amer. Chem. Soc.*, 1926, **48**, 882; Corrans, *Trans. Faraday Soc.*, 1927, **23**, 605.).

²⁴ Since no activation energy can be negative, the above difference indicates that the fast-stage of elimination has a finite activation energy (cf. footnote ²⁰).

the solvent "80 % EtOH" (a mixture of 80 vols. ethyl alcohol and 20 vols. water) are assembled in Table VII.

TABLE VII.*—ARRHENIUS PARAMETERS AND EXAMPLES OF THE EFFECT OF TEMPERATURE ON OLEFIN PROPORTION IN SUBSTITUTION WITH ELIMINATION IN "80 % EtOH" AS SOLVENT.

(i) Second Order Reactions.

Alkyl Derivative.	$k(S_N2)$		$k(E2)$		Temp.	$\frac{100E2}{S_N2 + E2}$
	$\log_{10} B_2$	$E(\text{kilocal.})$	$\log_{10} B_2$	$E(\text{kilocal.})$		
<i>iso</i> -PrCl (a)	9.4	23.0	10.7	24.8	$\begin{cases} 70^\circ \\ 90^\circ \end{cases}$	$\begin{cases} 57.1 \\ 60.6 \end{cases}$
<i>iso</i> -PrBr (b)	10.1	21.7	10.9	22.6	$\begin{cases} 50^\circ \\ 100^\circ \end{cases}$	$\begin{cases} 58.1 \\ 66.5 \end{cases}$

(ii) First Order Reactions.

	$k_1 = k(S_N1 + E1)$		Temp.	$\frac{100E1}{S_N1 + E1}$
	$\log_{10} B_1$	$E(\text{kilocal.})$		
<i>tert.</i> -BuCl (c)	11.9	23.1	$\begin{cases} 25^\circ \\ 65^\circ \end{cases}$	$\begin{cases} 16.8 \\ 36.3 \end{cases}$
<i>tert.</i> -AmCl (d)	11.9	22.9	$\begin{cases} 25^\circ \\ 50^\circ \end{cases}$	$\begin{cases} 33.0 \\ 40.3 \end{cases}$
<i>tert.</i> -Am ⁺ SMe ₂ (e)	17.2	31.6	$\begin{cases} 50^\circ \\ 83^\circ \end{cases}$	$\begin{cases} 47.8 \\ 53.7 \end{cases}$

* [(a) Hughes and Shapiro, *loc. cit.*⁸; (b) Hughes, Ingold and Shapiro, *loc. cit.*⁸; (c) Cooper, Hughes and Ingold, *loc. cit.*,¹⁰ and unpublished experiments; (d) Hughes and MacNulty, *loc. cit.*¹⁰; (e) Unpublished investigation by B. J. MacNulty.]

While there is as yet no satisfactory theoretical explanation of the precise nature of these effects of temperature, it is interesting to notice that the differences to which attention has been called are all in the direction in which they would be if solvation were the dominant cause, and if the apparent (Arrhenius) energy of activation were a good index of the real activation energy, *i.e.*, if the two varied in a parallel manner from case to case.

Thus, for the two bimolecular reactions, S_N2 and $E2$, of alkyl halides, the initial state is the same, whilst of the two activated states, that corresponding to elimination is less solvated because of its more widely distributed unit charge (*cf.* Table IV). Solvation would therefore operate to produce a greater activation energy for elimination than for substitution; and if this difference reappears in the apparent activation energies, as derived from the Arrhenius equation, then the elimination process must have the larger temperature coefficient, as is found experimentally.

Concerning the common slow stage of the unimolecular reactions, S_N1 and $E1$, the main difference between alkyl halides and 'onium salts is in their initial states, one of which is neutral while the other is charged. The expected strong solvation of the latter should lead to a larger activation energy for the heterolysis of 'onium ions than for that of alkyl halide molecules. This may be connected with the observed much larger apparent activation energies for the total first order reactions of sulphonium salts than for those of alkyl halides.²⁵

As to the fast stages of the separate first order reactions, here also a unit charge is distributed in the transition state, but more extensively in the process leading to elimination. Therefore by the argument in the last paragraph but one, the elimination must have the larger activation energy; and, if it also has the larger apparent activation energy, an increase of temperature will once again favour elimination, as is observed.

These explanations neglect the difficulties which arise when we continue to treat the Arrhenius critical energy as a true index to the actual energy of activation: and in order to give a fair picture of the state of the theory of temperature effects, we must mention these difficulties. They emerge in the form of a striking lack of connection between the apparent activation energy and structure in certain cases in which, no less than in most others, the reaction rate itself has a simple and intelligible relation to structure.

We know that certain groups of examples exist in which changes of structure produce changes of reaction rate which are reflected in approximately equivalent changes in the apparent energy of activation, the latter therefore having nearly as close a relation to structure as the former. This phenomenon, which has been widely illustrated in recent years, was first brought to light by Bradfield and Jones, who at the same time²⁶ discovered the further relationship that such activation energies are in first approximation additive functions of the variable substituents in the molecule. However, the large amount of attention which these phenomena have received seems to some extent to have obscured the circumstance that simple relations involving the apparent energy of activation are the exception rather than the rule. A striking example showing lack of relationship is at hand in the total first order reactions of corresponding *iso*-propyl and *tert*.-butyl halides: for readily intelligible reasons, the latter react about 10^4 times faster than the former, but the apparent activation energies are about the same.²⁷ It has been supposed²⁸ that apparent activation energies may exhibit simple relations when the effect of a distant structural change is communicated to the site of reaction through a connecting conjugated system. But even this possibly necessary condition may not be sufficient, as is indicated by the work of Conant on the reaction of iodide ions with alkyl chlorides.²⁹ Here also large changes of rate bear an intelligible relation to structure, but no discernible relation to the apparent energy of activation. It

²⁵ The ionic reactant is here a cation; it has been shown that a similarly increased apparent activation energy in unimolecular reactions arises when the reactant is an anion (Hughes and Taher, *J. Chem. Soc.*, 1940, 956).

²⁶ Bradfield and Brynmor Jones, *ibid.*, 1928, 1006.

²⁷ Hughes, *Trans. Faraday Soc.*, 1938, 34, 200.

²⁸ Ingold and Nathan, *J. Chem. Soc.*, 1936, 222.

²⁹ Conant and Kirner, *J. Amer. Chem. Soc.*, 1924, 46, 232; Conant and Hussey, *ibid.*, 1925, 47, 476; Conant, Kirner and Hussey, *ibid.*, p. 488.

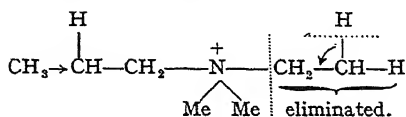
is clear from these examples that there are serious limitations to the extent to which we should use Arrhenius critical energies in lieu of real activation energies in theoretical arguments. It is only in the theory of temperature effects that, for lack of a feasible alternative, we do so. In all other branches of the theory of reaction mechanism we use the well-established principle that the rate-constant itself is more truly related to the chemical conditions than is its measured temperature coefficient.³⁰

(3) Constitutional Influences.

In 1851 Hofmann observed that, when a quaternary ammonium hydroxide contains different primary alkyl groups, so that various olefins might be produced by decomposition in different directions, the one actually formed is always ethylene if an ethyl group is present. Generalising this conclusion, we can restate it as indicating the preferential formation of that ethylene which carries the *smallest* number of alkyl groups. In 1875 Saytzeff noticed that, of the isomeric olefins which could be formed from a secondary or tertiary alkyl halide by elimination in the different branches of the alkyl chain, the one actually produced in the greatest proportion is determined by the condition that the hydrogen atom eliminated is lost preferentially from the least hydrogenated carbon atom. Otherwise expressed, this rule indicates the preferential production of that ethylene which carries the *largest* number of alkyl groups. Set side by side, especially in the light of our present-day recognition of the close analogy of the elimination reactions to which they respectively refer, these two generalisations of a bygone age are of much interest: they indicate that a substituent may influence elimination by two distinct internal mechanisms, which, moreover, are activated by forces of so independent a nature that the mechanisms may work in opposition. It will be our object to identify these internal mechanisms.

(3.1) The Hofmann Rule and the General Inductive Effect.—

The internal mechanism underlying the Hofmann rule was identified with the general inductive effect by Hanhart and Ingold in 1927. An elimination reaction always involves a strongly electron attracting group which, by inducing a positive charge on all the surrounding carbon atoms, loosens the protons, a sufficient loosening of a β -proton permitting the elimination mechanism E2. A group which, by releasing electrons, tends to neutralise the induced positive charge on the β -carbon atom, and thus to tighten its hold on the β -proton, will inhibit reaction. The terminal methyl radical of the *n*-propyl group acts in this way, and so determines that, in accordance with Hofmann's rule, the *n*-propyl group will show little tendency to engage in an olefin-forming process if an ethyl group is available to fulfil this function:



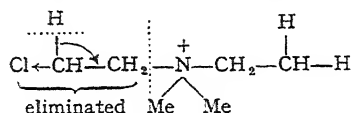
Similarly, an *isobutyl* group will not participate to any serious extent in elimination if a *n*-propyl (or ethyl) group is available; and,

³⁰ Evans and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 1333; Hughes, Ingold and Shapiro, *loc. cit.*²; Cooper and Hughes, *J. Chem. Soc.*, 1937, 1183.

naturally, the terminal methyl radicals in the *n*-propyl and *iso*-butyl groups may be replaced by ethyl or higher homologous radicals without changing these comparisons. This is the generalised rule given above, which was actually obtained from the theory, Hofmann's original empirical rule then being recognised as a special case.

Further generalisation follows from the consideration that the protective electron displacement can be relayed to the β -carbon atom from non-adjacent atoms, but only with considerable loss of intensity. Thus the protective effect to be observed in the *n*-propyl group will be greater in the *n*-butyl group, though not so great as in the *iso*-butyl group. In general the effect will increase with homology, tending to a limit, but always subject to the conditions that a branched chain radical is more effective than the isomeric normal chain.

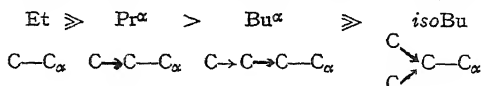
Outside the range of hydrocarbon radicals, we expect electron-attracting substituents to promote elimination, and to do so with particular effect if they are attached to the β -carbon atom :



With various degrees of completeness and elaboration, these deductions have been tested and established for a number of primary alkyl and substituted alkyl groups, not only for ammonium hydroxides and alkoxides,³¹ but also for sulphonium hydroxides,³² and for the alkali-promoted elimination reactions of sulphones.³³

Although the bimolecular mechanism was presupposed at the time of these experiments, no control was established over the reaction kinetics, the existence of the unimolecular mechanism being then unsuspected. However, the investigations were almost entirely concerned with alkaline decompositions involving primary alkyl groups, and subsequent research has shown that in these conditions the mechanism is, indeed, wholly bimolecular. The actual method of experiment was "orientational"; that is to say, the measurements related to the proportions in which products were formed in decompositions which could proceed in a number of alternative directions.

One form of this method was to place two olefin-forming alkyl groups in competition, as illustrated in the two preceding formulæ. In this way it has been shown, for instance, that in the decompositions of sulphonium hydroxides the first four primary alkyl groups stand in the following sequence with respect to the facility with which they split off as olefins; the large and small gaps between the members of the sequence are indicated by single and double inequality signs :



The graphic representations indicate the application of theory by the use of a thick arrow to mark a protective effect acting directly on the

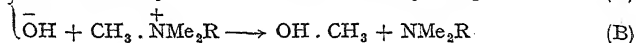
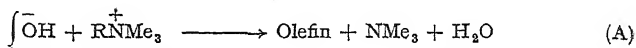
³¹ Hanhart and Ingold, *loc. cit.*¹; Ingold and Vass, *loc. cit.*¹; Ingold and Patel, *loc. cit.*¹

³² Ingold, Jessop, Kuriyan and Mandour, *loc. cit.*³; Ingold and Kuriyan, *loc. cit.*³




³³ Fenton and Ingold, *J. Chem. Soc.*, 1928, 3127; *ibid.*, 1929, 2338.

β -carbon atom, and a thin one to denote a corresponding effect of more distant origin and therefore greatly reduced intensity.

Another method of comparison employed 'onium ions containing only one olefin-yielding alkyl group, and assumed that changes beyond its β -carbon atom would not much affect simultaneous substitution at the carbon atom of a methyl group independently attached to the 'onium atom. The success of the elimination process with different olefin-yielding alkyl groups, in competition with this nearly standard substitution process, was taken as a measure of the intrinsic tendency of the variable group to yield an olefin. In the example



the following values were obtained for the percentage in which the olefin-forming process (A) participates in the complete decomposition ($\text{R} =$):

Et (95 %)	Pr α (84 %)	Bu α (79 %)	Am α (77 %)
C—C α	C→C—C α	C→C→C—C α	C→C→C→C—C α
Oct α (75 %)	isoAm (72 %)	isoBu (63 %)	ψ -Hex (43 %)
(C β)—C→C→C—C α	 C→C—C α	 C—C α	 C—C α

The comparison assumes that the variable group R does not engage in substitution to form an alcohol, and for cations RNMe_3^+ this is true to a high degree of approximation.

At a later time, when duality of mechanism for elimination generally, and the consequent need for kinetic control, had been realised, and particularly when a parallel investigation by the kinetic method into the basis of the Saytzeff rule had given results emphasising its contrast with the Hofmann rule, it was felt desirable to confirm kinetically that the rates of bimolecular olefin formation in ammonium and sulphonium compounds really did vary with homology in the sense indicated by theory and by the older orientational data. So far as primary alkyl groups are concerned, this has been done³⁴ for ethyl, *n*-propyl and *n*-butyl groups in the example of alkyltrimethylammonium ethoxides. In each case the constituent reactions (analogues of A and B above) are both of the second order. The rate constants (k_{E2} in $\text{sec}^{-1} \text{ g. mol}^{-1} \text{ l.}$) for olefin formation in dry ethyl alcohol at 100° are as follows:

R in RNMe_3^+	CH ₃ ·CH ₂	CH ₃ ·CH ₂ ·CH ₂	CH ₃ ·CH ₂ ·CH ₂ ·CH ₂
$10^5 k_{E2}$	8.9	0.72	0.47

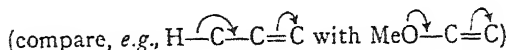
This illustrates how kinetic measurements substantiate the earlier conclusions. Further confirmation has been obtained by extending the kinetic study to include secondary and tertiary alkyl groups, but these results are more conveniently reserved for illustration later.

(3.2) The Saytzeff Rule and the Tautomeric Effect.—When in 1935 Baker and Nathan³⁵ adduced evidence for the view that CH-bond

³⁴ Unpublished investigation by F. R. Webb.

³⁵ *J. Chem. Soc.*, 1935, 1844.

electrons participate in tautomeric electron displacements, much in the manner of unshared electrons



though with considerably less freedom, it was not a difficult guess that this was the internal mechanism which was responsible for the elimination phenomena summarised under the Saytzeff rule. However, this idea could not at once be substantiated.

In the first place, the theory of Baker and Nathan had to establish itself against initial opposition.³⁶ We supported it from the outset, perceiving the part it was destined to play in the theory of organic reactions; and with Taher we have since helped to strengthen the evidence.³⁷ We believe that to-day the theory is generally accepted.³⁸

Secondly, numerous consequences of applying the theory to eliminations had to be tested by new experiments. This has now largely been done, although only a few of the results, and a limited discussion, have so far been published.³⁹

Just as in the preceding sub-section, we treated inductive electron displacement as the only effective internal mechanism, so in this sub-section we shall take the simplifying view that only the tautomeric effect need be considered; and we shall restrict illustrations to cases in which it is dominating. The problem of the co-existence of the two effects will be considered in the next sub-section.

In elimination, the tautomeric effect of alkyl groups arises essentially in the transition state of reaction. It involves, on the one hand, the electrons of γ -CH-bonds, and, on the other, those of the partly formed $\text{C}_\beta\text{C}_\alpha$ -double bond. The quasi-conjugation of these electrons modifies their wave functions in such a way as to give them a larger share of configuration space, and therefore a smaller energy.

This follows from the uncertainty principle, and is typical of the quantal effects which are customarily summarised as resonance (Fig. 3). The result is a reduction of the energy of the transition state, and therefore of the activation energy, with a corresponding facilitation of the elimination process.

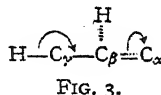


FIG. 3.

We have to supplement this theory in one respect. According to Baker and Nathan's original principle, the resonance effect of an alkyl group attached to unsaturated carbon would be large with methyl, but would diminish and finally disappear in the series ethyl, *isopropyl* and *tert.*-butyl, owing to the progressive loss of suitably situated CH-bonds. It has since been suggested,⁴⁰ however, that, even with the *tert.*-butyl group, a residual resonance effect will be found, and that in other cases a part of the total observed effect is not dependent on CH-bonds. This is because of the expectation that when two atoms of identical nuclear charge are linked, the electrons will concentrate in the direction of the

³⁶ See report of an early discussion on the subject, *Chem. and Ind.*, 1936, 55, 962.

³⁷ *J. Chem. Soc.*, 1940, 949; a summary of literature is given in this paper.

³⁸ Mulliken's recent quantal calculation (*J. Amer. Chem. Soc.*, 1941, 63, 41) seems to us to warrant this statement.

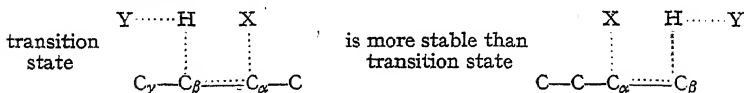
³⁹ Hughes, Ingold, Masterman and MacNulty, *J. Chem. Soc.*, 1940, 908; Hughes and Ingold, *Nature*, 1941, 147, 812.

⁴⁰ Hughes, Ingold, Masterman and MacNulty, *loc. cit.*³⁹

less saturated, because this gives them freer motions, thereby stabilising the system in accordance with the uncertainty principle. The extended theory is naturally quite general, though we are here concerned only with its application to the transition state in eliminations.

The expected consequences of this tautomeric or resonance effect differ strikingly from those of the inductive or electrostatic effect considered earlier. In the latter connection we assumed mechanism E2, and, in order to make the comparison definite, we may now do the same, although the following conclusions may be applied also to the rapid stage of mechanism E1. (a) On account of the tautomeric effect, an alkyl radical attached to the β -carbon atom of the complete alkyl group should facilitate its degradation to an olefin. (b) Since either end of the incipient double bond is equally available for quasi-conjugation, alkyl radicals attached to the α -carbon atom of the complete alkyl group should exert an effect similar to that just mentioned. (c) The effect produced by a methyl radical attached to either the α - or the β -carbon atom should be decreased when methyl is replaced by ethyl and higher primary radicals, and decreased still more when secondary or tertiary radicals are substituted.

Inference (a), applied differentially to unequal branches in an unsymmetrical secondary or tertiary alkyl group, leads to Saytzeff's rule. Thus the more stable of the transition states which could arise from a *sec.*-butyl compound will be that which has a methyl radical attached to the β -end of the $\alpha\beta$ -unsaturated bond, the final ethylene carrying two alkyl groups, instead of only one:



Of course, Saytzeff's rule is not so general as the theoretically based inference (a), which may be used to compare alkyl groups of different molecules, including primary and symmetrically branched secondary and tertiary alkyl groups, concerning which the Saytzeff rule has nothing to say. Conclusions (b) and (c) are also clear extensions of the original empirical rule.

We may draw one more conclusion: (d) There is nothing in the theory which restricts its application to alkyl groups. We have noted how a methyl radical, by engaging in quasi-conjugation with the developing double bond, assists its formation. Obviously, a stronger effect of the same kind is to be expected if the methyl radical is replaced by an unsaturated, and therefore properly conjugated, radical such as phenyl. The theory is, indeed, general for unsaturated and pseudo-unsaturated substituents.

It naturally became necessary to test the general conclusions of the theory by a comparative kinetic study of the elimination reactions of alkyl halides, including primary and symmetrically branched secondary and tertiary halides, under conditions in which the bimolecular and unimolecular mechanisms of elimination could be kinetically separated and distinguished. This has been done with respect to a considerable number of alkyl halides. The figures^{40, 41} selected for inclusion in Table VIII furnish the simplest illustration of the main points.

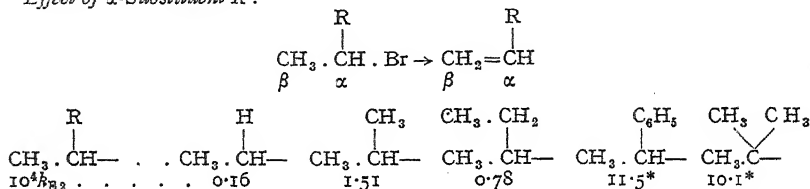
⁴¹ Unpublished investigations by M. L. Dhar and S. Masterman.

The rate constants given in this Table relate to uniform conditions, and all refer to bimolecular elimination processes (E2). The figures illustrate (a) facilitation by a β -linked methyl radical, (b) facilitation by an α -linked methyl radical, (c) the diminished acceleration produced by an ethyl radical in either position, and (d) the increased acceleration produced by a phenyl radical in either position. We also see the effect of methyl repeated on the introduction of a second methyl substituent.

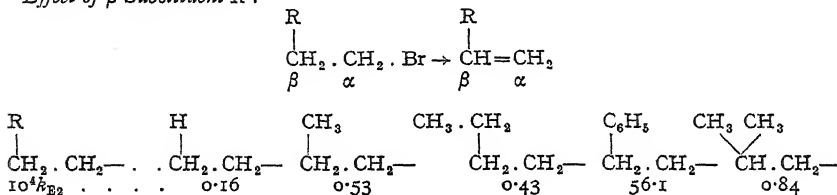
TABLE VIII.—RATE CONSTANTS (k_{E2} IN SEC.⁻¹ G.-MOL.⁻¹ L.) FOR SECOND ORDER ELIMINATION REACTIONS OF ALKYL HALIDES.

(Conditions : ~ 0.1 N-NaOEt in anhydrous EtOH at 55°)

Effect of α -Substituent R :—



Effect of β -Substituent R :—



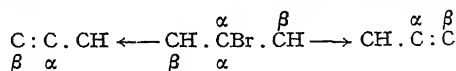
(* Estimated from measurements at larger ionic strengths.)

The further point may be noted that the methyl radical exerts a larger effect from the α -position, whilst the phenyl radical acts more strongly from the β -position. This may be a result of the simultaneous presence of the electrostatic effect, which becomes important in the case of β -linked substituents, and for methyl opposes the resonance effect, but for phenyl supports it (owing to the Ar-C link dipole).

Some examples showing the way in which the velocity effects illustrated above combine together to produce orientational results in secondary and tertiary alkyl halides,⁴² are assembled in Table IX. Here also the conditions are uniform, and the second order olefin reaction has been kinetically isolated; but the rates are now given in the form of the separate parts which correspond to elimination along the different branches of the alkyl groups. These partial rates are entered against the corresponding alkyl branches on either side of the formulæ, and associated with each figure is a note of the substituents attached to the α - and β -ends of the double bond formed, the labels α and β relating as before to the carbon atoms from which halogen and hydrogen respectively are lost.

Comparing the first and second entries, one sees (left-hand columns) that, in agreement with theory, the extra β -Me radical in the second example accelerates the formation of Δ^2 -butene as compared with its

⁴² Unpublished investigation by M. L. Dhar.

TABLE IX.—RATE CONSTANTS (k_{E2} IN SEC.⁻¹ G.-MOL.⁻¹ L.) DETERMINING ORIENTATION IN SECOND ORDER ELIMINATION REACTIONS OF SECONDARY AND TERTIARY ALKYL HALIDES.(Conditions: ~ 1.0 *N*-NaOEt in anhydrous EtOH at 25°.)

Substituents		$10^6 k_{E2}$ per Branch.		$10^6 k_{E2}$ per Branch.	Substituents	
α	β				α	β
Me	—	1.18	CH ₃ . CHBr . CH ₃	1.18	Me	—
Me	Me	2.86	CH ₃ . CH ₂ . CHBr . CH ₃	0.61	Et	—
Me	Et	1.96	CH ₃ . CH ₂ . CH ₂ . CHBr . CH ₃	0.80	<i>n</i> -Pr	—
Et	Me	2.00	CH ₃ . CH ₂ . CHBr . CH ₂ . CH ₃	2.00	Et	Me
			CH ₃ . CH ₂ . CHBr . CH ₂ . CH ₃	10.0	Me ₂	—
Me ₂	—	10.0	CH ₃ . CBr $\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$	10.0	Me ₂	—
Me ₂	Me	42.0	CH ₃ . CH ₂ . CBr $\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$	8.5	MeEt	—
				8.5	MeEt	—

lower homologue, whilst (right-hand columns) the replacement of α -Me by α -Et retards the formation of Δ^1 -butene. Both rate changes contribute to produce a strong orientating effect (4.69 : 1) of the Saytzeff type. Comparing the second and third entries, we find (left), again in agreement with theory, that the replacement of β -Me by β -Et retards the formation of Δ^2 -pentene in comparison with Δ^2 -butene, whereas (right) the replacement of α -Et by α -Pr, which in theory should have little influence, actually slightly accelerates the formation of Δ^1 -pentene in comparison with Δ^1 -butene. The result is still an orientation which agrees with the Saytzeff rule; but it is decidedly weaker (2.45 : 1) in the pentene case, contrary to what might naïvely have been assumed in view of the greater dissymmetry of the amyl bromide molecule. In such a manner the theory accommodates a number of fine details, which are not expressed in any empirical rule.

We may interpolate a reference here to the differential influence of alkyl structure on elimination and substitution in the second order reactions of alkyl halides, and to the consequential effect on the proportion of olefin formed. Considering first the successive introduction of α -linked methyl substituents, we know that, in the series Et, Pr^{*β*}, Bu^{*γ*}, the rate of bimolecular substitution decreases; and we have just seen that the rate of bimolecular elimination increases; therefore the proportion of olefin, $E2/(S_{N2} + E2)$, must increase strongly. With regard to successively introduced β -linked methyl radicals, we know that, in the series Et, Pr^{*α*}, *iso*Bu, the rate of bimolecular substitution falls, though not very greatly; and we noticed above that the rate of bimolecular elimination rises, but again less strongly than before; therefore the proportion of olefin will exhibit an increase, which, however, will be less pronounced than that produced by α -linked methyl radicals. The following figures^{41, 42} may be quoted to illustrate these variations:—

	$\text{CH}_3 \cdot \text{CH}_2 \cdot (\text{CH}_3)_2\text{CH} \cdot (\text{CH}_3)_3\text{C} \cdot$	
	Decreasing S_N2	
	Increasing E_2	
Percentage Olefin (in EtOH at 25°)	1	80 ~ 100
	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_3 \cdot \text{CH}_2 \cdot (\text{CH}_3)_2\text{CH} \cdot \text{CH}_2 \cdot$	
	Decreasing S_N2	
	Increasing E_2	
Percentage Olefin (in EtOH at 55°)	1	9 60

Different relations will naturally obtain for the bimolecular reactions of 'onium salts, whose eliminations are controlled essentially by the general inductive, rather than by the tautomeric, effect.

The first order elimination reactions of alkyl halides show generally similar effects of structural changes in the alkyl groups on the rates of the component reactions, though the effects on the whole are larger. Correspondingly the orientation in unimolecular elimination is still of the Saytzeff type, but is on the whole stronger than in the bimolecular process.

Because of the two-stage nature of the unimolecular mechanism, the rate constant k_{E1} is composite, and this has to be borne in mind when using it for the purpose of judging constitutional effects. It is the product of the rate of ionisation, and the fraction of the formed carbonium ion which completes an elimination. From some points of view this fraction, that is, the percentage of olefin formed is more simply related to structure than is the rate of elimination. Some secondary alkyl bromides⁴² are compared below, with respect to the percentage of olefin they yield; the solvent is "60 % EtOH," that is, a mixture of 60 volumes of ethyl alcohol and 40 volumes of water, and the temperature is 80°:—

$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CHBr} \\ \diagup \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \cdot \text{CH}_2 \\ \diagdown \\ \text{CHBr} \\ \diagup \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \cdot \text{CH}_2 \\ \diagdown \\ \text{CHBr} \\ \diagup \\ \text{CH}_3 \cdot \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \\ \text{CHBr} \\ \diagup \\ \text{CH}_3 \end{array}$
4.6 %	8.5 %	14.7 %	6.9 %

Even though data are not available which would permit the figures for the two unsymmetrical compounds to be split up into parts corresponding to reaction in the alternative branches of the alkyl chain, it is obvious that a β -methyl substituent facilitates the completion of elimination, that a β -ethyl radical does so less strongly, and that the effect or both alkyl substituents is more marked than in second order elimination.

A comparison of the proportions of olefin formed in the first order reactions of isopropyl and *tert.*-butyl bromides⁴⁶ shows that an α -methyl substituent in the alkyl chain is even more effective than a β -methyl substituent in directing the process towards elimination.

A comparison in terms of rates is given for two tertiary halides in Table X. The figures⁴² may be compared with those given for the second order reactions of the same compounds in Table IX. The data on the left of either Table show a qualitatively similar influence: the extra β -Me substituent in the higher homologue accelerates the formation of the Δ^2 -isopentene, though the effect is larger in the unimolecular mechanism. However, the figures on the right of the two Tables reveal a difference: the replacement of α -Me₂ by α -MeEt, which retarded formation of the Δ^1 -isopentene in the bimolecular reaction, is associated

with an increase in the rate of its production by the unimolecular mechanism. This apparent anomaly is immediately explained by the mechanistic difference: the rate constant k_{E1} contains as a factor the rate of ionisation of the alkyl halide, which is about twice as great for *tert.*-amyl as for *tert.*-butyl bromide; allowance being made for this, the structural effects of the substituents α -Me₂ and α -MeEt assume a normal relationship.

TABLE X.—RATE CONSTANTS (k_{E1} IN SEC.⁻¹) DETERMINING ORIENTATION IN FIRST ORDER ELIMINATION REACTIONS OF TERTIARY ALKYL HALIDES.

(Conditions: Neutral or acidic, anhydrous EtOH at 25°)

Substituents α β		10 ⁶ k_{E1} per Branch.		10 ⁶ k_{E1} per Branch.	Substituents α β	
α	β				α	β
Me ₂	—	0.29	$\begin{array}{c} \text{CH}_3 \diagup \\ \text{CH}_3 \cdot \text{CBr} \\ \text{CH}_3 \diagdown \end{array}$	0.29	Me ₂	—
				0.29	Me ₂	—
Me ₂	Me	3.22	$\begin{array}{c} \text{CH}_3 \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CBr} \\ \text{CH}_3 \diagdown \end{array}$	0.37	MeEt	—
				0.37	MeEt	—

(3.3) Co-existence of the General Inductive and Tautomeric Effects.—At one time it seemed curious that two rules of such contrary tendencies as the Hofmann and Saytzeff rules should govern different parts of the field of the elimination reactions of alkyl compounds; and we have been at pains to determine whether the distinction is due to the nature of the alkyl compound, 'onium ion or halide, or to the type of alkyl group, primary, secondary or tertiary, or to the mechanism of reaction, bimolecular or unimolecular. The results of our survey, summarised in Table XI, show that the determining circumstance is a combination of the first and third of these factors. Bimolecular 'onium salt reactions are subject to the Hofmann rule. Bimolecular reactions of halides, and also unimolecular reactions, whether of 'onium salts or

TABLE XI.—RANGE OF CONTROL OF HOFMANN AND SAYTZEFF RULES (H AND S) IN THE ELIMINATION REACTIONS OF ALKYL COMPOUNDS.

Mechanism.	'Onium Ions			Halides		
	Prim.	Sec.	Tert.	Prim.	Sec.	Tert.
E ₂	H	(H)*	H	S	S	S
E ₁	—	S	S	—	S	S

(* Investigation incomplete.)

halides, are governed by the Saytzeff rule. The course of unimolecular reactions would naturally be independent of whether the intermediate carbonium ion arises from an alkyl 'onium ion or an alkyl halide.

The remarkable effect of crossing the boundary between the regions

of control of these two rules in the case of 'onium salts may be illustrated by reference to *tert.*-butyl- and *tert.*-amyl-dimethylsulphonium ions.⁴³ As shown in the top left-hand corner of Table XII, the rate of elimination under bimolecular conditions is smaller for the higher homologue; moreover, the mixture of amylenes produced has a composition corresponding to the Hofmann rule. Under suitably changed conditions unimolecular reactions supervene and now, as shown in the bottom left-hand corner of the Table, the rate of elimination becomes greater for the higher homologue; furthermore, the composition of the amylenes is inverted to one conforming to Saytzeff's rule.

TABLE XII.—RATE CONSTANTS AND ORIENTATION IN SECOND AND FIRST ORDER ELIMINATION REACTIONS OF *tert.*-ALKYLDIMETHYLSULPHONIUM IONS.

Second Order. (Conditions: "97.5 % EtOH" at 24.3°. Units: k_{E2} in sec.⁻¹ g.-mol.⁻¹ l.)

Group.	Total $10^4 k_{E2}$	Olefin Composition (%)		Partial $10^4 k_{E2}$		Partial $10^4 k_{E2}$
		CHMe:CMe ₂	CMeEt:CH ₂			
Bu ^y	6.93	—	—	2.31	CH ₃ · C(⁺ SMe ₂) $\begin{cases} \text{CH}_3 \\ \text{CH}_3 \end{cases}$	2.31 2.31
Am ^y	5.09	14	86	0.70	CH ₃ · CH ₂ · C(⁺ SMe ₂) $\begin{cases} \text{CH}_3 \\ \text{CH}_3 \end{cases}$	2.20 2.20

First Order. (Conditions: "80 % EtOH" at 65.3°. Units: k_{E1} in sec.⁻¹)

	Total $10^3 k_{E1}$			Partial $10^3 k_{E1}$		Partial $10^3 k_{E1}$
Bu ^y	4.21	—	—	1.40	CH ₃ · C(⁺ SMe ₂) $\begin{cases} \text{CH}_3 \\ \text{CH}_3 \end{cases}$	1.40 1.40
Am ^y	29.5	85	15	25.1	CH ₃ · CH ₂ · C(⁺ SMe ₂) $\begin{cases} \text{CH}_3 \\ \text{CH}_3 \end{cases}$	2.21 2.21

The right-hand side of the Table shows the partial rates for elimination along each of the branches of the tertiary alkyl groups. The figures for bimolecular conditions (top) exhibit a relationship not previously illustrated. The extra β -linked methyl substituent reduces the rate of elimination in the long branch of the *tert.*-amyl chain in accordance with the idea that the electrostatic effect is dominant. On the other hand, the rate of elimination in the shorter branches, which would have been reduced in the higher homologue had the resonance effect been in control (*cf.* Table IX), is scarcely altered; and this also is consistent, since, for elimination in these directions, the structural change is in an α -linked group, and is too far removed from the β -hydrogen atom to affect it appreciably by the electrostatic mechanism. The partial rates for the unimolecular mechanism (bottom) exhibit a relationship closely similar

⁴³ Unpublished investigation by L. I. Woolf.

to that already illustrated and discussed in the case of the analogous alkyl halides (*cf.* Table XI).

Such results as these throw light on less fully investigated reactions. Thus the dehydration of alcohols in the presence of acids or of iodine is known to obey the Saytzeff rule.⁴⁴ For the reaction catalysed by iodine, the further point has been established that tendency to elimination

along an alkyl branch $R \cdot \overset{\beta}{CH_2} \cdot \overset{\alpha}{C}$ varies with R according to the order $H \ll Me > Et, Pr^x$, etc. For the same reaction, the olefin formed from *tert.*-amyl alcohol has been shown to have a similar composition to that which we have found for reactions of *tert.*-amyl compounds known to proceed by the unimolecular mechanism. The catalysts suggest oxonium intermediates, and a comparison of the results mentioned with our data for sulphonium salts strongly suggests that the intermediates undergo elimination by the unimolecular mechanism (Fig. 4).

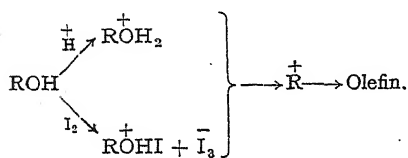


FIG. 4.

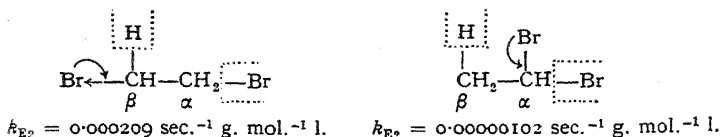
It can scarcely be doubted that the demonstrated existence of separate fields of control by the general inductive and tautomeric effects on the velocity and orientation of the elimination reactions of alkyl derivatives is to be taken to mean that, in principle, both effects are al-

ways present, but that, owing to circumstances still to be considered, either one or the other dominates. Several apparent indications of a modifying influence of the minor effect on a broad result determined by the major one are to be found on close inspection of the data: an instance was noticed in the preceding sub-section (p. 677). However, if we go outside the field of alkyl groups, and examine, on the one hand, more polar groups, and, on the other, more unsaturated groups, then inductive or tautomeric effects as the case may be, which would have been masked in simple alkyl compounds, can be made to dominate.

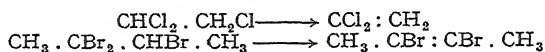
For example, we know that second order eliminations of alkyl halides obey the Saytzeff rule, and are controlled essentially by the tautomeric internal mechanism; any influence due to the inductive internal mechanism is at best slight, and is in any case difficult to discern. However, if we introduce into the alkyl group a powerfully electron-attracting β -halogen substituent, then the elimination reaction of the β -halogenoalkyl halide is very greatly accelerated. We can show that this is not a tautomeric effect, due to conjugation of the unshared halogen electrons with the developing double bond, although this would produce an acceleration. For the tautomeric effect should work just as well from the α -position, and therefore, if we take the corresponding α -halogenoalkyl halide, instead of the unsubstituted alkyl halide, as the standard of comparison, we shall isolate the general inductive effect, which is primarily a property of β -linked substituents. This was what Olivier and Weber⁴⁵ did when they made the following comparison of the rate of two reactions leading to vinyl bromide (solvent, a mixture of 1 volume of acetone with 3 volumes of water; temperature, 30°):—

⁴⁴ Whitmore and Evers, *J. Amer. Chem. Soc.*, 1933, **55**, 812; Whitmore and Rothrock, *ibid.*, p. 1106; Church, Whitmore and McGrew, *ibid.*, p. 1528; Thompson and Sherril, *ibid.*, 1936, **58**, 745.

⁴⁵ Olivier and Weber, *Rec. trav. chim.*, 1934, **53**, 1087; Olivier, *ibid.*, p. 1093.



The larger rate associated with the β -bromo-substituent shows that, owing to the strong polarity of the group, the general inductive effect is in control, though it would not have been in a simple alkyl halide. Olivier assumed a controlling electrostatic effect, and (whilst not attempting to reconcile the Saytzeff rule with it) pointed out that it correctly interpreted numerous orientational results relating to the elimination reactions of polyhalogeno-paraffins. The following is a pair of examples selected for contrast:—



The rule is always that, of the hydrogen atoms which could be eliminated in association with the various halogen atoms, the one actually eliminated is that attached to the most halogenated, and therefore most positive, carbon atom. Similar evidence convinced Olivier that the carboxyl group directs the course of eliminations by means of its electrostatic effect.

There is evidence of a complementary kind concerning the incursion of the tautomeric effect into the bimolecular eliminations of 'onium salts, where, for simple alkyl derivatives, the general inductive effect controls the reaction. The phenyl group in β -phenylethyl-ammonium and -phosphonium compounds, and in corresponding sulphones, accelerates elimination to an extent which we may ascribe to the powerful effect of conjugation.⁴⁶ Upon this tautomeric effect, a general inductive effect has again been superimposed in the example of *p*-nitro- β -phenylethylammonium salts,⁴⁷ which undergo bimolecular decomposition with extraordinary ease, presumably on account of both the unsaturation of the aryl group and the polarity of the nitro-group.

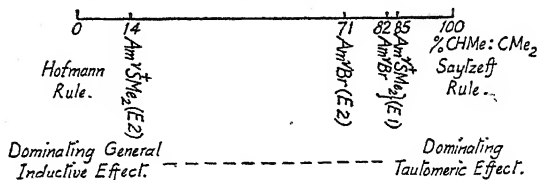
These facts show that the general inductive and tautomeric effects jointly influence elimination, their relative importance depending on the polarity and unsaturation of the influencing group. But when both the polarity and unsaturation are small, as with alkyl groups, the relative importance of the two effects can be seen to depend also, indeed primarily now, on the system which is being influenced. Let us consider this factor.

We know that when, in the bimolecular mechanism, the influenced system is of the form $\text{HC} \cdot \underset{\beta}{\text{C}} \cdot \overset{+}{\underset{\alpha}{\text{X}}} \text{ (X = N or S)}$, the inductive effect dominates; and that when it is of the type $\text{HC} \cdot \underset{\beta}{\text{C}} \cdot \overset{+}{\underset{\alpha}{\text{Hal}}}$, the tautomeric effect takes charge; whilst when, in the unimolecular mechanism, it is $\text{HC} \cdot \overset{+}{\underset{\beta}{\text{C}}} \cdot \overset{+}{\underset{\alpha}{\text{C}}}$ (sextet), once more the tautomeric effect is in control. Moreover, the quantitative results show that the predominance of the tautomeric effect is greater in the last case: we find larger effects on reaction rate, and more extreme orientation of the Saytzeff type, in unimolecular

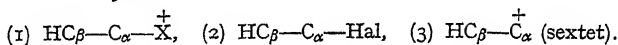
⁴⁶ Hanhart and Ingold, *loc. cit.*¹; Fenton and Ingold, *J. Chem. Soc.*, 1929, 2338; *ibid.*, p. 2342; Hughes and Ingold, *loc. cit.*¹

⁴⁷ Hanhart and Ingold, *loc. cit.*¹; Hughes and Ingold, *loc. cit.*¹

elimination with either 'onium salts or halides than in bimolecular elimination with halides. Taking the single illustration of the composition of the mixed amylenes formed from *tert.*-amyl compounds, we may express the gradations diagrammatically, thus:—



Empirically then, the tautomeric effect increases in relative importance as the system influenced takes the successive forms:—



From a theoretical point of view, the differences must arise from a balance between the intensity of the positive charge induced on C_β , which calls out the general inductive effect of attached alkyl groups, $\text{Alk} \rightarrow \text{C}_\beta$, and the degree of unsaturation developed in the transition state, which stimulates the tautomeric effect of the quasi-conjugation,

$\text{H---C}_\gamma\text{---}\overset{\curvearrowright}{\text{C}}_\beta\text{---}\overset{\curvearrowright}{\text{C}}_\alpha$. We can see at once that the general inductive effect will be greater in (1) than (2), because of the stronger electrostatic effect of the free pole. Also we may reasonably expect the tautomeric effect to be greater in (2) than in (1), because solvation assists the heterolysis of the C---Hal bond, but not of the $\text{C---}\overset{+}{\text{X}}$ bond; wherefore the transition state of (2) tends to involve a relatively large electron-transfer in order to form the charges needed to produce the solvation energy. Obviously the tautomeric effect will be much greater in (3) than in either (1) or (2), because of the intense unsaturation created by the pre-formed sextet; however, the general inductive effect will also be much greater in (3), because of the proximity of the carbonium ionic centre to C_β . Putting these points together, we see that it is possible to understand the large difference between (1) and (2), although theory is ambiguous with respect to the smaller difference between (2) and (3).

Thus for eliminations we envisage a situation very similar to that recognised long ago in the field of aromatic substitution: general inductive and tautomeric effects co-exist, and are separately energised, the one by electrostatic forces, the other by quantal resonance; therefore they are independent, and, when superimposed, they may either collaborate or act in opposition. In aromatic substitution this conception was used to reconcile the non-parallelism of orientation and reaction rate. In elimination we have used it to reconcile contrary orientation rules, and establish their consistency with reaction rate. In both fields the tautomeric mechanism has been found to exert its main effect in the transition state of reaction ("polarisability effect"). Other analogies can be found, which suggest that the considerations now advanced regarding eliminations tend towards the unification of the theory of organic reactions in general.

In this essay we have concentrated attention on the most fundamental of all possible types of elimination, namely 1 : 2-elimination from

saturated compounds. A good deal of collatable evidence exists with regard to 1:1-elimination involving dimerisation, and 1:3-elimination involving molecular rearrangement, and the various categories of elimination which are associated with ring formation; the same is true with respect to the numerous types of elimination possible for unsaturated compounds. On the other hand, it is only for the simplest form of elimination, 1:2-elimination from saturated compounds, that experimental investigation has entered upon a quantitative phase, with the result that it has become possible to build up a reasonably clear theoretical picture of the process, its principal mechanisms, and the factors which influence them. This is the reason for the restriction we have placed on the present discussion, and for our decision to leave to a future occasion the connected consideration of more complicated elimination processes.

We desire to thank Professor T. Campbell James for the continued hospitality of his laboratory.

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GENERAL DISCUSSION

Dr. A. Wassermann (*London*) said: Difficulties similar to those mentioned by Hughes and Ingold in section (2.4) of their paper arise if an attempt is made to give a theoretical interpretation to the results of certain equilibrium measurements, for it has been observed that the equilibrium constant itself has sometimes a more discernible relation to chemical conditions than either the entropy change or the heat change.

Dr. W. A. Waters (*Durham*) said: In assessing solvent effects in bimolecular heterolytic substitutions the transition state may be regarded as a tripole, $\bar{Y} \dots \overset{+}{R} \dots \bar{X}$, with an electrostatic energy $= \frac{3}{2} \cdot \frac{\epsilon^2}{D \cdot d}$ which is formed from initial reactants, \bar{Y} , and $R-X$ which have a total electrostatic energy $\left(\frac{1}{2} \cdot \frac{\epsilon^2}{D \cdot r} + \frac{\mu^2}{2\alpha} \right)$ where r is the radius of the ion \bar{Y} , and μ the dipole moment and α the bond polarisability of the dipole $R-X$. Since Hughes, Ingold and their collaborators have shown experimentally that the rate of a bimolecular substitution is but little affected by changing the solvent it follows that d for the tripole is of the same order of magnitude as r .

The electrostatic energy change in a unimolecular reaction is $\left(\frac{\epsilon^2}{D \cdot d'} - \frac{\mu^2}{2\alpha} \right)$ where d' is the distance of separation of the charges in the activated state $\overset{+}{R} \dots \bar{X}$.

By putting $d = d'$ (approx.) one can deduce that, in regard to the electrostatic energy change on activation, a bimolecular reaction should require more energy than a unimolecular reaction if $r > d$ and vice-versa. Hence, in favouring any particular mechanism of substitution, the dielectric effect of a solvent should be of less significance than its associative properties in forming solvate complexes with ions and polar molecules. The value of d' for the activated structure is not just the bond length, but is dependent upon the extent of polarisation of the bond $R-X$ by the organic groups constituting R .

In reply to a query by Prof. Ingold, Dr. Waters stated that measurements of anion radii and of covalent bond lengths indicated that r and d were almost equal for the alkyl halides.

Dr. Hughes, in reply, said: The conclusion, that the dielectric constant of a solvent (or even a simpler measure, such as the dipole moment, of the longer-range forces of its molecules) is of less importance for the formation of solvates than associative power derived from local molecular fields, has previously been emphasised by us, though without the mathematical support which Waters now adduces.¹

¹ Cf. for example Bateman, Hughes and Ingold, *J. Amer. Chem. Soc.*, 1938, 60, 3080.

MECHANISM AND KINETICS OF CARBOXYLIC ESTER HYDROLYSIS AND CARBOXYL ESTERIFICATION.

BY J. N. E. DAY AND C. K. INGOLD.

Received 4th September, 1941.

Arrangement.

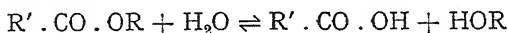
1. Multiplicity of Mechanism.
2. Bimolecular Basic Hydrolysis with Acyl-oxygen Fission.
3. Unimolecular and Bimolecular Basic Hydrolysis with Alkyl-oxygen Fission.
4. Unimolecular and Bimolecular Acid Hydrolysis and Esterification with Acyl-oxygen Fission.
5. Unimolecular and Bimolecular Acid Hydrolysis and Esterification with Alkyl-oxygen Fission.

(1) Multiplicity of Mechanism.

One of the more general results of the recent study of reaction mechanism has been the discovery that certain reactions, even those which have usually been considered to be amongst the simplest in organic chemistry, may pursue any of several mechanisms. In carboxyl esterifications and hydrolysis we have a reaction which is not altogether simple; and, consistently, a number of distinct mechanisms may be recognised. Furthermore, since the experimental study of the reaction is still in a somewhat primitive stage, we may not assume that all the existing homogeneous mechanisms have yet been discovered.

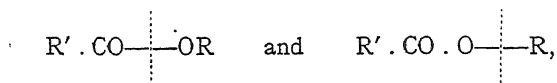
For the purpose of classifying the available mechanisms we may consider three features of the reaction. The most immediately recognisable guide is the nature of the reagent. We know that esters may be hydrolysed by alkalis or by acids, and many circumstances convince us that different mechanisms, or groups of mechanisms, apply in these two cases. A less well-known form of hydrolysis occurs in neutral solution, and this can be shown not to be a simple extrapolation to a weakly basic or weakly acidic reagent of ordinary alkaline or acid hydrolysis. Thus it would appear that there are three main groups of mechanisms; but we shall regard two of these groups as more closely related to each other than to the third. For in both alkaline and

neutral hydrolysis the two-oxygen entity which engages in reaction with the third oxygen atom in the stoicheiometric equation

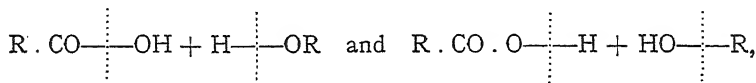


is certainly the neutral $R' \cdot CO_2R$, whilst in acid hydrolysis it is the ion $[R' \cdot CO_2HR]^+$. The same sub-division is in principle applicable to esterification. Alkaline esterification is rendered impossible by the stability of the carboxylate ion. Neutral esterification is just conceivable, but has not so far been realised: if it were realised the reacting two-oxygen entity would be $R' \cdot CO_2H$. Acid catalysed esterification is well known, and the reacting entity is $[R' \cdot CO_2H_2]^+$. Thus for both hydrolysis and esterification we make our main division of mechanisms according to whether or not a preliminary proton transfer to the carboxyl compound is necessary for the reaction (this somewhat too restricted statement is generalised in the sequel).

In order to elaborate this classification we turn to a second diagnostic feature, namely, the position of rupture of the carboxyl compound. There are several different methods of determining this, one general and the others limited, but all so easy to operate that the result need never remain unknown. For hydrolysis the possible modes of rupture are



and it is convenient to name them. Since the bonds broken are respectively the acyl-oxy-bond and the alkyl-oxy-bond, we may refer to "acyl-oxygen fission" and "alkyl-oxygen fission." For esterification the corresponding alternatives are



and we shall retain the same two names. Now it is found that for alkaline hydrolysis acyl-oxygen fission is the rule, whilst for neutral hydrolysis alkyl-oxygen fission prevails. Thus, within the main group of mechanisms for which the attacked entity is the neutral molecule, $R' \cdot CO_2R$, there are two sub-groups differentiated from each other by the position of rupture of the ester grouping. It has further been found that in acid catalysed hydrolysis and esterification, in which the attacked entity is the ion, $[R' \cdot CO_2HR]^+$ or $[R' \cdot CO_2H_2]^+$, either acyl-oxygen fission or alkyl-oxygen fission may take place according to circumstances. Thus, on application of this second criterion, our original two-fold classification of mechanisms becomes four-fold.

Having assigned a mechanism to its class, the final step must be to elucidate its nature as completely as possible by means of the third, and most powerful, of the available diagnostic methods, namely, the study of the reaction kinetics. This is an intensive and detailed matter, which has not yet been carried so far as with the substitution and elimination reactions of saturated compounds. Nevertheless it does appear, from the limited amount of work which has been done, that, within certain of the classes, two mechanisms exist which are related to each other just like the bimolecular and unimolecular mechanisms of substitution or of elimination. On account of the analogy we shall

refer to such mechanisms as "bimolecular" or "unimolecular": it is by now a commonplace that such names are essentially labels (given according to a certain plan), and have no simple and general implication with respect to reaction order.

It is convenient to summarise our classification here, noting the mechanisms which have so far been established or indicated.¹ This is done in Table I, which will be useful as a guide to the arrangement of the remainder of this paper. In order to develop a convenient notation, we symbolise "basic" mechanisms, including the alkaline and related neutral mechanisms, in which the entity attacked is the neutral molecule, by the letter B; and "acidic" mechanisms, in which an oxonium cation is degraded, by the letter A. One and two dashes are used to denote fission of the acyl-oxy- and alkyl-oxy-bonds respectively, whilst as usual the figures 1 and 2 indicate whether the mechanism is of the unimolecular or bimolecular type.

TABLE I.—MECHANISMS OF CARBOXYLIC HYDROLYSIS AND ESTERIFICATION.

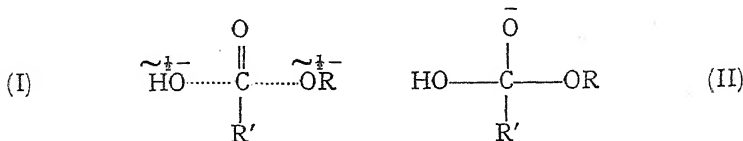
Type of Mechanism.	Entity Attacked.	Known Reactions.	Type of Fission.	
			Acyl-oxy-	Alkyl-oxy-
Basic	$R' \cdot CO_2R$	Hydrolysis only	$\left\{ \begin{array}{c} \text{—} \\ B'_2 \end{array} \right.$	$\begin{array}{c} B''_1 \\ B''_2 \end{array}$
Acidic	$\left\{ \begin{array}{c} (R' \cdot CO_2HR)^+ \\ (R' \cdot CO_2H_2)^+ \end{array} \right.$	$\left. \begin{array}{c} \text{Hydrolysis} \\ \text{Esterification} \end{array} \right\}$	$\left\{ \begin{array}{c} A'_1 \\ A'_2 \end{array} \right.$	$\begin{array}{c} A''_1 \\ A''_2 (?) \end{array}$

We may conclude this section with what will be a generally approved caution against attempting theoretical distinctions between varieties of a mechanism that could not be distinguished experimentally. This point is mentioned because the recent literature provides several instances in which a known mechanism, instantly recognisable when reduced to its simplest terms, has reappeared in such a form that considerable scrutiny is necessary in order to discover that it does not contain some entirely new idea. Almost any mechanism may be elaborated by the introduction of unnecessary proton movements. Some can be varied by the addition of inessential hydrations and dehydrations. But, unless such elaborations can be shown to lead to some observable chemical effect, one prefers to omit them. References to recent examples to both these forms of "disguise" could be given.

However, the most subtle distinction without a difference arises when corresponding intermediates vary only with respect to their electron distributions. Consider, for instance, the attack of \bar{OH} on the carbon atom of the group $\cdot CO_2R$. The reaction might be represented either on the model of a nucleophilic substitution, or on that of a nucleophilic carbonyl addition. Which model we use at any particular time depends on the analogies we desire to emphasize, but the point now to be made is that the mechanisms so expressed are identical, although one might have been tempted to suppose that mechanisms based on substitution and addition would be fundamentally different. The identity becomes

¹ They were first brought into relation with one another by Datta, Day and Ingold (*J. Chem. Soc.*, 1939, 838) and Hughes, Ingold and Masterman (*ibid.*, p. 840).

apparent when we examine the expressions (I) and (II) for the most condensed intermediate state :

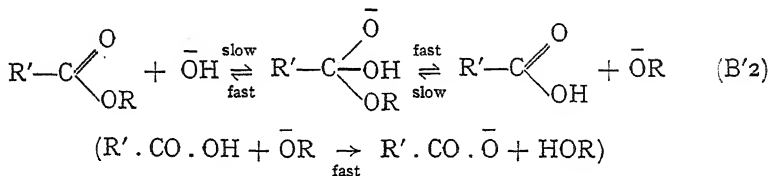


These differ only in electron distribution, and are clearly to be regarded as imperfect representations of a mesomeric system having an intermediate electronic arrangement.

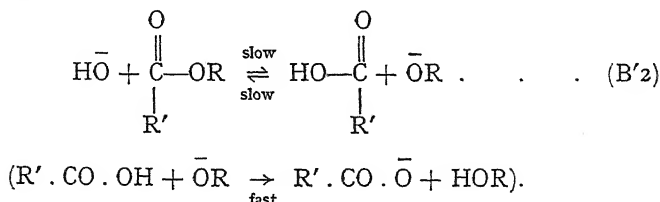
With these preliminaries we may proceed to discuss in turn the four groups of mechanisms indicated by the subdivisions of Table I.

(2) Bimolecular Basic Hydrolysis with Acyl-oxygen Fission (B'2).

The hydrolysis of carboxylic esters by hydroxide ions in aqueous solvents is known to be a reaction of the second order, and all experiments on the location of the attack agree in indicating the acyl-oxygen bond as the one which is broken in the reaction. Theory suggests only one mechanism consistent with these observations, namely the bimolecular mechanism :



The process is in principle reversible, but in practice is driven completely to the right by the final proton transfer from the formed carboxylic acid to the alkali of the solution. We have here used the second and more familiar of the previously mentioned methods of expressing this mechanism, but we know that the represented intermediate must to some extent partake of the nature of the transition state of the pure substitution process



This representation of mechanism B'2 is the more convenient for purposes of comparison with the other mechanisms of hydrolysis and esterification.

The crux of the argument in support of mechanism B'2 is the demonstration that fission occurs according to the scheme $\text{R}' \cdot \text{CO} - \text{OR}$. Holmberg was the first to produce clear evidence of acyl-oxygen

fission in alkaline hydrolysis.² He used a form of R, which was asymmetric at the point of attachment, and assumed that, if R were to separate from this point in the course of reaction, R would not retain its configuration. In the example of O-acetyl malic acid he showed that the asymmetric group did retain its configuration. All that we have since learnt of the Walden inversion shows that Holmberg's basic assumptions and deduction were correct.

Subsequently other methods were devised. Ingold and Ingold³ selected a form of R which, if liberated, would be mesomeric and would therefore yield an isomeric alcohol. Crotyl and α -methylallyl are forms of R for which this is true, and Prévost⁴ had shown that acetates containing these radicals R were hydrolysed by alkali without isomerisation.

These methods are limited by the necessity for choosing a special form of R, but the following method, due to Polanyi and Szabo,⁵ is general. They employed water whose oxygen is distinguished by the presence of an enhanced proportion of the heavier isotopes; and they showed, in the example of the alkaline hydrolysis of amyl acetate, that oxygen from such a medium does not enter into the alcohol, and therefore must enter into the acid formed by hydrolysis. This result clearly demands fission of the link which binds oxygen to the acyl residue.

The most recent method,⁶ a limited one, is based on Whitmore's conclusion that the neopentyl radical, if liberated as a cation, undergoes a rearrangement leading to *tert.*-amyl compounds and amylene. It was observed that neopentyl esters such as the acetate undergo alkaline hydrolysis normally, without giving *tert.*-amyl alcohol or amylene.

The first of the expressions for mechanism B'2 depicts addition of the attacking anion. It is consistent that alkaline hydrolysis demands strong electron recession from the seat of reaction, as is shown by the effect of polar substituents on the reaction rate.⁷ As with all bimolecular processes, the reaction shows considerable sensitivity to steric inhibition by α -substituents, and, in the case of benzoic esters, by ortho-substituents.⁷

Dawson has shown⁸ that acetate and bisulphate ions make a small but definite contribution to the rate of hydrolysis of ethyl acetate in buffer solutions. The additional reaction responsible for the rate increase may well have a mechanism analogous to B'2, the product, a mixed anhydride, undergoing subsequent rapid hydrolysis. Similarly amide formation from esters and ammonia, and radical exchange between esters and alkoxides, may pursue mechanisms analogous to B'2. It is important to appreciate, however, that such mechanistic extrapolations are highly hypothetical and often dangerous, since we know so

² Holmberg, *Ber.*, 1912, 45, 2997.

³ Ingold and Ingold, *J. Chem. Soc.*, 1932, 758.

⁴ Prévost, *Ann. Chim.*, 1928, 10, 147.

⁵ Polanyi and Szabo, *Trans. Faraday Soc.*, 1934, 30, 508.

⁶ Norton and Quayle, *J. Amer. Chem. Soc.*, 1940, 62, 1170.

⁷ Skrabal and Hügetz, *Monatsh.*, 1926, 47, 17; Skrabal and Rückert, *ibid.*, 1928, 50, 369; Smith and Olsson, *Z. physikal. Chem.*, 1925, 118, 99; Olsson, *ibid.*, 1925, 118, 107; 1927, 125, 243; 1928, 133, 233; Kindler, *Annalen*, 1926, 450, 1; 1927, 452, 90; 1928, 464, 278; *Ber.*, 1936, 69, 2792; Ingold and Nathan, *J. Chem. Soc.*, 1936, 222; Evans, Gordon and Watson, *ibid.*, 1937, 1430; 1938, 1439; Tommila and Hinshelwood, *ibid.*, 1938, 1801.

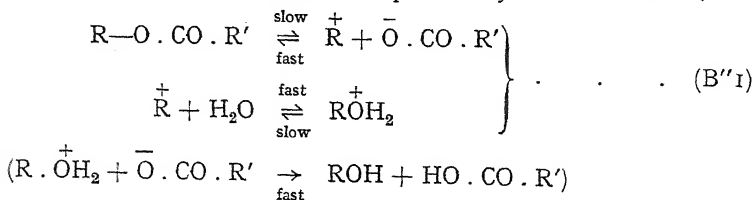
⁸ Dawson and Lowson, *ibid.*, 1927, 2444; 1929, 394; Dawson, Pycock and Spivey, *ibid.*, 1933, 291.

many reactions, even reactions between closely analogous factors to give closely analogous products, which nevertheless proceed by entirely different mechanisms; indeed, we know that the same individual reaction may often pursue different mechanisms in not very drastically altered circumstances.

(3) Unimolecular and Bimolecular Basic Hydrolysis with Alkyl-oxygen Fission (B'1 and B'2).

The ester molecule contains two carbon atoms, viz., the α -carbon atoms of the acyl and alkyl groups, which are indicated by analogy to be in principle susceptible to attack by nucleophilic reagents: $R'C_{\alpha}O \cdot OC_{\alpha}R''_3$. However, one of these atoms is unsaturated and the other is saturated; and it is perhaps natural that the unsaturated atom should be the more powerful competitor for the reagent, with the result, as we have seen, that acyl-oxygen fission is the general rule. We shall imagine, nevertheless, that, with the hydroxide ion as the nucleophilic reagent, two reactions, which we may shortly describe as acyl attack and alkyl attack, occur side by side, although the former is much the faster, and therefore the only observable process. Let us suppose now that the hydroxide ion is replaced step-wise by progressively weaker nucleophilic reagents: then both acyl attack and alkyl attack will be reduced in speed, although always acyl attack will remain the faster process. Assuming a suitable structure for the group CR''_3 , and a suitable solvent, there will be a certain finite rate of ionisation

of the ester $R' \cdot CO \cdot OCR''_3$ into $R' \cdot CO \cdot \bar{O}$ and $\overset{+}{C}R''_3$; and, as the nucleophilic reagent is weakened, first the rate of alkyl attack and then that of acyl attack will fall below the rate of the ionisation. At this latter crossing of rates we pass from a bimolecular reaction associated with acyl-oxygen fission to a unimolecular mechanism involving alkyl-oxygen fission—from mechanism B'2 to mechanism B'1. We are concerned essentially with hydrolysis, not with all the possible reactions analogous to hydrolysis, and hence the two nucleophilic reagents in which we are chiefly interested are the hydroxide ion and the water molecule. Therefore the significant conclusion is that, if the structure of the alkyl group and the ionising power of the solvent are such that the described change of mechanism occurs before the nucleophilic reagent has been so far weakened as to become a water molecule, then, although alkaline hydrolysis will pursue mechanism B'2, hydrolysis in neutral solution will proceed by mechanism B'1:—

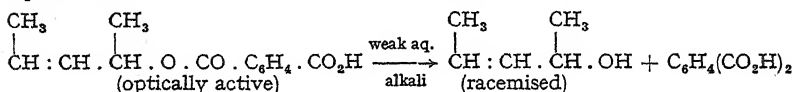


The mechanism is in principle reversible, although the final proton transfer from the alkyloxonium ion to the carboxylate ion will in practice drive it almost completely in the direction of hydrolysis.

The recognisable characteristics of this mechanism are that it exhibits the proper kinetics, and that it is associated with alkyl-oxygen

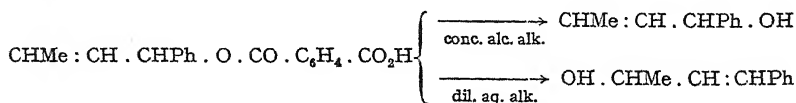
fission. In particular, the group R, if asymmetric at the point of attachment, should become racemised, and if $\beta\gamma$ -unsaturated, should become isomerised, in the course of the reaction. The reaction should require electron release by R, and electron withdrawal by R', and should not be sensitive to steric hindrance (*vide infra*).

The experimental evidence for this process is fragmentary but highly significant: it is due to Kenyon and his associates, who drew the conclusion that the liberation of the cation $\overset{+}{R}$ is involved. Their form of R consisted of $\alpha\gamma$ -dialkyl or -arylalkyl substituted allyl groups, which are known to have a strong tendency to pass into cationic forms. The immediate problem was the preparation of optically active alcohols of these radicals by hydrolysis of the resolved hydrogen phthalates. It was found⁹ that α -methylcinnamyl and $\alpha\gamma$ -dimethylallyl hydrogen phthalates, on hydrolysis in very weakly alkaline solutions, gave fully racemised alcohols, although hydrolysis with concentrated alkali yielded optically active alcohols. The inference is that the reaction with concentrated alkali is largely a bimolecular hydrolysis (B'2), involving, therefore, acyl-oxygen fission, and hence producing no racemisation; but that in very weak alkali the rate of this second order process is so far reduced as to leave in complete control the unimolecular mechanism (B''1), which, since it involves alkyl-oxygen fission with separation of R as a cation, leads to racemisation:



Although this interpretation seems very possible, it would, of course, be most desirable kinetically to separate the alkaline and neutral reactions, and to study the stereochemical course of each in kinetically controlled conditions.

Further confirmation arises in connection with the α -phenyl- γ -methylallyl group, which, if liberated as a cation, should on account of its mesomerism produce an isomeric alcohol. It was observed¹⁰ that α -phenyl- γ -methylallyl hydrogen phthalate, on hydrolysis with concentrated methyl alcoholic alkali, gave only its own alcohol; but that if the solvent were made more aqueous, and especially if the alkalinity were reduced also, the main alcoholic product was the isomeric γ -phenyl- α -methylallyl alcohol:



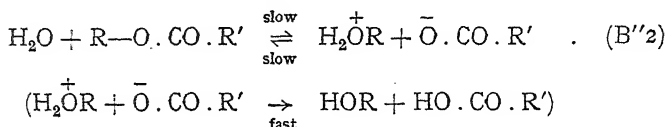
An interpretation is that the change of conditions has produced a change of mechanism: with much alkali and a poor ionising solvent, mechanism B'2 predominates, whilst with reduced alkalinity and a good ionising solvent mechanism B''1 assumes control. This is the same experimental test which Ingold and Ingold applied to the alkaline aqueous hydrolysis of α -methylallyl acetate, with the result that this reaction was shown to pursue mechanism B'2 alone; but applied to a

⁹ Kenyon, Partridge and Phillips, *J. Chem. Soc.*, 1936, 85; Hills, Kenyon and Phillips, *ibid.*, p. 582.

¹⁰ Kenyon, Partridge and Phillips, *ibid.*, 1937, 216.

case involving a more strongly electron releasing alkyl group, as well as a more strongly electron attracting acyl group, the same test indicates that mechanism B''I may supervene under suitable physical conditions. Once again kinetic control should be applied before this last inference is accepted.¹¹

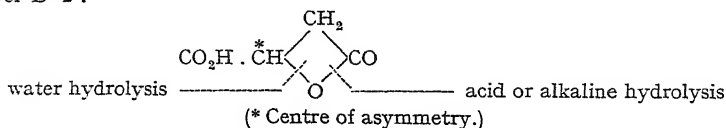
According to the explanation given of the relationship between mechanisms B'2 and B''I, the remaining mechanism of basic hydrolysis, B''2, that is, bimolecular attack by a nucleophilic reagent on the alkyl carbon atom, would appear to be incapable of experimental realisation. Actually it has been realised, but only under quite special circumstances. In the known examples the reagent is the water molecule, and we formulate the mechanism for this case:



The process may be regarded as in principle reversible, although the final proton transfer from the alkyloxonium ion to the carboxylate ion will direct it in practice almost completely from left to right. There is no indication of the appearance of this mechanism with hydroxide ion as the nucleophilic reagent.

Mechanism B''2 may be recognised by the characteristic that if R is asymmetric at the point of attachment, hydrolysis will be accompanied, not merely by racemisation, but by an optical inversion at the asymmetric centre.

The existence of mechanism B''2 was first demonstrated in this way during an elucidation of the somewhat complicated stereochemical changes which accompany the hydrolysis of the halogenosuccinic acids.¹² An intermediate product of these hydrolyses is β -malolactonic acid, which can be isolated, and is shown to undergo hydrolysis to malic acid by three distinct mechanisms. In either concentrated or dilute alkaline solution the reaction is very rapid and preserves configuration; in quite dilute acid it is slow and inverts configuration; in more concentrated acid it is faster and retains configuration. The first of these reactions corresponds to mechanism B'2, and the third to mechanism A'2; both involve acyl-oxygen fission and therefore a retention of configuration. "However (to quote from the paper cited), in the absence of any alkali, and of sufficient acid to give adequate speed to the intrinsically rather slow process of acid hydrolysis, it becomes possible to observe a bimolecular displacement of the acyloxy-group by a water molecule, a process which must involve inversion." This is the mechanism we now label B''2:



¹¹ When Hughes, Ingold and Masterman predicted the existence of mechanism B''I (numbered VII in their paper) they had not noticed the records of the observations now referred to, and were thus unable to cite any supporting evidence. Our attention was called to these records by Dr. E. D. Hughes, and by Dr. M. P. Balfe.

¹² Cowdrey, Hughes, Ingold, Masterman and Scott, *J. Chem. Soc.*, 1937, 1264.

One other case has since been discovered, namely, that of β -butyrolactone (the above carboxyl group is replaced by methyl).¹³ The observed phenomena are exactly as described for β -malolactone, and a similar explanation has been applied.

Why the only two recorded appearances of this rare mechanism both relate to β -lactones it is hardly possible to say in any detail. But it can be understood in general terms that, since ring strain tends to make a saturated carbon atom in some respects more like an unsaturated one, the normal difference of reactivity between the α -alkyl and α -acyl carbon atoms, on the basis of which we might have inferred that mechanism B''2 would never appear, becomes in these lactones so far reduced that either position may be attacked if the reagent and conditions are appropriately chosen.

(4) Unimolecular and Bimolecular Acid Hydrolysis and Esterification with Acyl-oxygen Fission (A'1 and A'2).

We deal in this section with the acid catalysed formation and hydrolysis of esters, with the exclusion of a certain less important group of cases, which need not now be precisely specified since they are to be considered in section 5.

The two acid catalysed reactions are, of course, the reverse of each other, and, following almost all previous writers, all, at least, since Lapworth (1904), we shall assume that their mechanisms completely correspond, each being a reversal of the other. The similar orders of magnitude of the rates, and their parallel variation with the structure of the acyl and alkyl groups clearly point to this conclusion.

Recently a third reaction has been shown to be analogous to both acid hydrolysis and esterification, *viz.*, the acid catalysed oxygen exchange (using isotopically distinguished oxygen) between carboxylic acids and water. Herbert and Lauder first suggested,¹⁴ and Roberts and Urey supported the idea,¹⁵ that this reaction is to be regarded as an "esterification" of the carboxylic acid with water instead of alcohol. The rates of this reaction are also of the order of magnitude of those of the corresponding esterifications and hydrolyses.

In these acid catalysed hydrolyses, esterifications and oxygen exchanges it is the acyl-oxy-linking which is broken. This is self-evident in the case of oxygen exchange; and it has been fully established by the normal methods for hydrolysis and esterification.

This was first done by Holmberg² for acid hydrolysis by the method which seeks to detect any change of configuration in an alkyl group R which is asymmetric at its point of attachment in the ester. He showed that in the acid hydrolysis of O-acetyl malic acid, the asymmetric group completely retains its configuration. Recently a similar demonstration has been given for esterification in the example of the formation of β -*n*-octyl acetate.¹⁶

The method of choosing a form of R which, if liberated, would be mesomeric, and would accordingly lead to isomeric end-products, was

¹³ Olson and Miller, *J. Amer. Chem. Soc.*, 1938, **60**, 2690.

¹⁴ Herbert and Lauder, *Trans. Faraday Soc.*, 1938, **34**, 1219; *Nature*, 1938, **142**, 954.

¹⁵ Roberts and Urey, *J. Amer. Chem. Soc.*, 1939, **61**, 2584.

¹⁶ Hughes, Ingold and Masterman, *loc. cit.*¹.

applied by Ingold and Ingold³ to both acid hydrolysis and esterification in the example of the esters α -methylallyl acetate and crotyl acetate: no isomerisation was observed.¹⁷

The general method of using isotopically distinguished oxygen in one of the interacting oxygen compounds, and tracing its reappearance in one of the products, has been applied to acid hydrolysis in the examples of methyl hydrogen succinate¹⁷ and benzhydriyl formate.¹⁸ Oxygen from the water employed for the hydrolysis passed into the acid and not into the alcohol. The same method has been applied to esterification in the example of the formation of methyl benzoate.¹⁹ Here oxygen from the methyl alcohol passed into the ester and not into the water formed by the reaction. All these results prove acyl-oxygen fission.

Before proceeding to a consideration of more detailed evidence, we may set down the mechanisms, suggested by theory, which are consistent with the elementary circumstances already mentioned. So many proposals of this nature have at various times been made, that it may seem surprising that we reduce the number of acceptable alternatives to two. But we are pursuing the policy, indicated in section I, of seeking always the chemically significant meaning beneath different modes of expression. We therefore disregard distinctions dependent on such factors as facile intramolecular proton and electron movements; and, indeed, we neglect all other unverifiable elaborations of any fundamental mechanism. For instance, we treat as identical those mechanisms in which corresponding intermediates differ only in having protons attached to different oxygen atoms, and, as a corollary, we would regard as trivial the separation of a proton transfer into two stages by the provision of an intermediate stepping-stone for the proton.

Both our mechanisms involve a pre-equilibrium with an adding proton: they differ in what afterwards happens to the oxonium ion thus formed. According to the suggestion originally put forward by Ingold and Ingold,³ the oxonium ion first undergoes a rate-controlling heterolytic fission,²⁰ exactly as a sulphonium ion would in a unimolecular substitution (S_N1). Then a hydroxylic molecule rapidly attacks the formed carbonium ion, just as in the final stage of a unimolecular substitution. Lastly a proton, equivalent to that originally taken up, is split off. All proton transfers are regarded as effectively instantaneous. We formulate the mechanism in a reversible manner, so that, read forwards, it applies to hydrolysis, and, backwards, to esterification. The character (so to speak) of the mechanism lies in the two middle stages, and, on account of their correspondence to the two stages of unimolecular substitution, we call the mechanism "unimolecular,"²¹ and label it $A'1$:

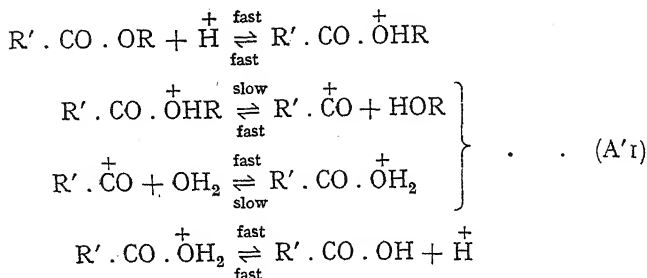
¹⁷ Datta, Day and Ingold, *loc. cit.*¹.

¹⁸ Unpublished experiments by P. Sheel.

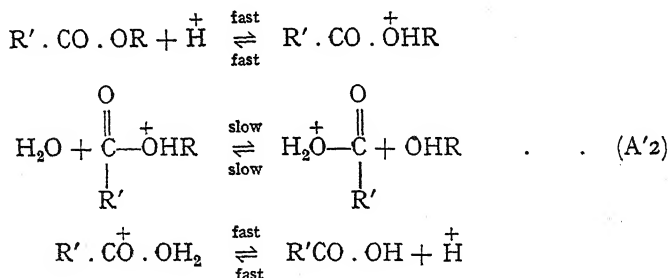
¹⁹ Roberts and Urey, *J. Amer. Chem. Soc.*, 1938, 60, 2391.

²⁰ The terms "homolysis" and "heterolysis" have been defined (*Trans. Faraday Soc.*, 1938, 34, 227) as bond fission according to the schemes $A \cdot \cdot B$ and $A \cdot \cdot \cdot B$ respectively (the dots represent electrons), independently of the charges on A and B and of any concomitant covalency changes.

²¹ The rule of nomenclature is that the expressed molecularity shall be equal to the number of molecules necessarily involved in covalency change in the rate-determining stage (Bateman, Church, Hughes, Ingold and Taher, *J. Chem. Soc.*, 1940, 1008).



The second mechanism can be derived from this exactly as we derive bimolecular substitution from unimolecular substitution: the mean life of the acylium ion is regarded as being reduced until it is of the order of a collision period; then the two stages, which previously represented the formation and destruction of this ion, become fused into a single bimolecular process. The initial proton uptake and the final proton loss are both fast reversible reactions as before. The characteristic stage of the mechanism is the middle one, and on account of its analogy with bimolecular substitutions, *e.g.*, of sulphonium and ammonium salts, we describe the mechanism as "bimolecular" and label it A'2:



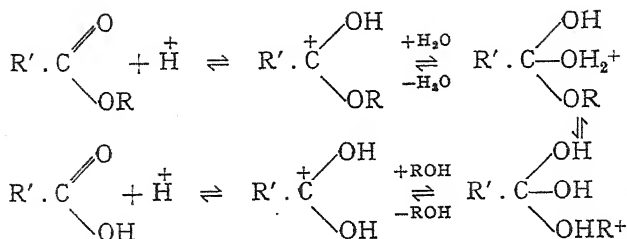
Mechanism A'2 differs very little from a mechanism which was suggested by Watson,²² although he expressed it in a very different form.²³ Datta, Day and Ingold¹⁷ put the mechanism into its present form, and brought it into relation with mechanism A'1. They mentioned also that mechanisms intermediate between A'1 and A'2 could be envisaged, much as with ordinary nucleophilic substitution.²⁴

It is of interest to trace the connection between our A'2 and Watson's expression, which is as follows:

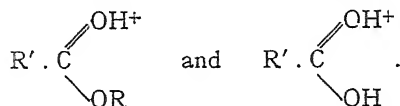
²² Watson, *Modern Theories of Organic Chemistry*, p. 130 (Oxford, 1937). Water's views (*J. Chem. Soc.*, 1936, 1014), though developed from Lowry's theory (*vide infra*), do not seem very dissimilar.

²³ Mechanisms identical with A'2, as well as with B'2, except for unimportant elaborations, have recently been advanced by Mumm (*Ber.*, 1939, 72, 1874).

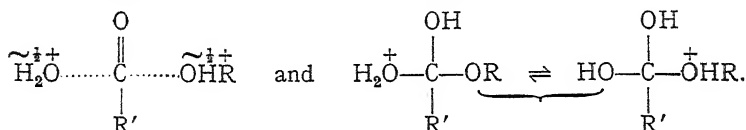
²⁴ Unfortunately, Datta, Day and Ingold tried to economise paper by representing mechanisms A'1 and A'2 in a single set of formulae with an attached footnote calling attention to the essential duality of the conception. This footnote has obviously been overlooked by Roberts and Urey,¹⁶ who accordingly missed the broader significance of the formulae, and were thereby led to make an inapplicable criticism of the views expressed by Datta, Day and Ingold.



In the first place, we may well prefer to replace Watson's carbonium ions by the intrinsically more stable oxonium ions,



The change is only in the representation of a mesomeric electron distribution, and it permits comparison with the first and third stages of our A'2. Next, if we consider the most condensed intermediate state of the system, we find that the comparison is between



These systems differ only in the position of a mobile proton, and in their electronic distribution, and these are differences we do not regard as crucial. It is true that the question may one day arise, whether the most condensed intermediate state occurs at the energy maximum or before or after it; but such distinctions are not in the present programme.

There are two types of previously proposed mechanism which are not equivalent to A'2 (or to A'1), but which we do not regard as acceptable. One is the group of termolecular mechanisms, of which the typical example is Lowry's.²⁵ It is generally understood how a termolecular mechanism can be derived by the synchronisation of two bimolecular reaction stages. What we have to do in order to derive Lowry's mechanism from our A'2, or from Watson's practically equivalent expression, is to synchronise the first two stages of either. That is to say, the approach of the proton to the ester (or acid) molecule has to be reduced in speed until it keeps pace exactly with the approach of the water (or alcohol) molecule, the synchronised double approach now determining the measured rate of reaction. This, however, is not at all in harmony with the modern idea, for which a great deal of support exists, that proton transfers between acidic and basic oxygen are very rapid processes, and cannot in general be retarded to conform to any rate which is measurable at ordinary temperature. The other class of mechanisms which we reject, as an obvious corollary of the above, comprises those, hitherto advanced (so far as we know) only

²⁵ Lowry, *J. Chem. Soc.*, 1925, 1381; *Trans. Faraday Soc.*, 1928, 24, 546.

by Roberts and Urey,¹⁵ which consist of bimolecular stages, but make a proton transfer the rate-determining stage.²⁶

From this review of other suggestions we return to the mechanisms A'1 and A'2. Both presuppose catalysts sufficiently strongly acidic in nature actually to transfer protons to the carboxylic acid or ester. Acids as strong as, or stronger than, H_3O^+ can probably be assumed to do this. Catalysis by weak acids will be referred to later.

The unimolecular mechanism, A'1, may be expected to be favoured relatively to the bimolecular process, A'2, by two principal factors. The first need is for a sufficiently powerful electron release from the radical R' to give reasonable stability to the acylium ion. Aryl radicals would be expected to be valuable in this connection. *Ortho*- and *para*-situated methyl groups should be of considerable assistance, on account of their capacity for quasi-conjugation (preceding paper) :



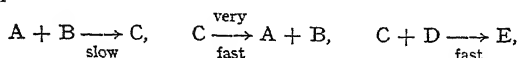
Correspondingly placed methoxyl groups should be still more effective were it not for their tendency to pass into oxonium forms in strongly acid conditions.

The second necessity for mechanism A'1 is a good solvent for the heterolysis of the acidium or esterium ion, $[\text{R}'\cdot\text{CO}\cdot\text{OH}_2]^+$ or $[\text{R}'\cdot\text{CO}\cdot\text{OHR}]^+$. The best known solvent is sulphuric acid, and, no doubt, the reason for its usefulness is its great affinity for the water or alcohol, OH_2 or OHR , which forms one of the heterolytic fragments. Water and alcohol themselves are, as might be expected, poor solvents for this fission. In preparative esterifications sulphuric acid is often used in such proportions that it may be regarded as a solvent, or, at least, an important constituent of the solvent.

The first direct evidence of the existence of mechanism A'1 was obtained by Treffers and Hammett,²⁷ who proved cryoscopically that the 2 : 4 : 6-trimethylbenzoyl cation is quite stable in concentrated sulphuric acid, and is formed rapidly and completely when 2 : 4 : 6-trimethylbenzoic acid is dissolved in that solvent (van't Hoff's factor $i = 4$) :

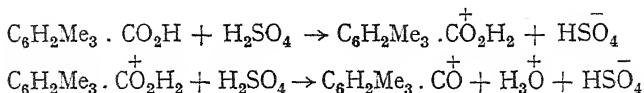
²⁶ It seems desirable to suggest some reason why Roberts and Urey, after a detailed and careful argument, reached so unacceptable a conclusion. The chief reason, we think, is that they were writing under the preconception that all the known phenomena of acid hydrolysis and esterification were referable to a single mechanism : the idea of duality or multiplicity of mechanism was simply not in their picture. Naturally they were hard pressed to find single mechanisms which appeared to satisfy the conditions imposed.

As a possible subsidiary reason, we may refer to their postulate, on which the whole kinetic argument was based, that the order of a reaction determines the reactants entering into the composition of the transition state of the slowest stage. This, however, is only conditionally true, one condition being that the reaction must not contain reversible stages ; it cannot be assumed generally true for reactions which, like acid hydrolysis and esterification, contain, and even consist entirely of, reversible stages. Consider, in illustration, the very simple system



the relative rates being as shown. The slow stage is the first, and the reactants in its transition state are A, B ; but the over-all reaction rate is proportional to $[\text{A}][\text{B}][\text{D}]$. The non-agreement of molecularity and order in this example is evidently due to the reversibility of the first stage of reaction.

²⁷ Treffers and Hammett, *J. Amer. Chem. Soc.*, 1937, 39, 1708.



With some other methyl substituted benzoic acids the indication was that the formation of the carbonium ion was substantial but incomplete ($2 < i < 4$). In benzoic acid itself the initial proton transfer was complete, but the formation of carbonium ion was insufficient for cryoscopic detection ($i = 2$).

The parallel behaviour of esters, and its importance in connection with hydrolysis, were indicated by the observation of the same authors that a freshly made solution of methyl 2:4:6-trimethylbenzoate, on being immediately poured into water, gave a quantitative precipitation of 2:4:6-trimethylbenzoic acid, whereas methyl benzoate, on similar treatment, remained almost wholly unhydrolysed. This result forms a striking contrast to the well-known retarding effect of ortho-substituents, including methyl substituents, in the acid hydrolysis of esters in aqueous solvents, or in the esterification of acids in alcoholic media. The difference is a clear indication of duality of mechanism, and its direction is in harmony with the idea that the reaction is unimolecular (A'1) in sulphuric acid, but bimolecular (A'2) in aqueous or alcoholic solvents. For, as we have seen, the strongly electron-demanding heterolysis, on which mechanism A'1 is dependent, is greatly assisted by the electromeric effect of the ortho-methyl substituents; whilst, as Hughes has pointed out in the first of these communications, unimolecular reactions in general are not sensitive to steric hindrance, because there is no particular congestion of bonds in the transition state of a heterolytic fission, the attack being more or less external, and the forces largely electrostatic. On the other hand, in the bimolecular mechanism, A'2, the electromeric effect of the methyl groups is very much less powerful, because of the much smaller electron-demand of this reaction, the rate-determining stage of which involves compensating electron transfers; whereas the steric effect of ortho-substituents is now very important, because of the inevitable congestion of bonds in a bimolecular transition state, the intimate character of the attack, and the generally greater importance of covalency than of electrostatic forces.

In the reactions of the trimethylbenzoic acid and its ester in sulphuric acid, the formation of the acylium ion is rapid and complete; but the production of such an ion need be neither rapid nor complete in order that it may constitute an intermediate for mechanism A'1. In those cases in which the rate of hydrolysis or esterification can be measured, the heterolysis must, indeed, be slow, since its rate controls that of the measured reaction; the stationary concentration of the acylium ion might be very low.

The main kinetic requirements of mechanism A'1 are that the initial rate of hydrolysis shall be proportional to $[\overset{+}{\text{H}}]$ [Ester], and the initial rate of esterification to $[\overset{+}{\text{H}}]$ [Acid], the former rate being independent of water and the latter of alcohol. There is a distinction here from mechanism A'2, which requires the initial rate of hydrolysis to be proportional to $[\overset{+}{\text{H}}]$ [Ester] $[\text{H}_2\text{O}]$, and of esterification to $[\overset{+}{\text{H}}]$ [Acid] $[\text{ROH}]$. With sulphuric acid as solvent the factor $[\overset{+}{\text{H}}]$ may be treated as constant,

for the proton transfer is complete; but the distinction between the two mechanisms with respect to the appearance or otherwise of water and alcohol in the expressions for initial reaction rate remains. The hydrolysis of methyl benzoate under these conditions has been studied kinetically.²⁸ With small concentrations of the reagents the rate is of first order with respect to ester and of zeroth order with respect to water, as required by mechanism A'1. With large concentrations of water the rate is diminished, owing to the inhibition of the mechanism as the heterolytic power of the solvent is impaired.

We have already noted some of the main characteristics of the bimolecular mechanism, A'2, which prevails for hydron-catalysed hydrolysis and esterification in aqueous and alcoholic solvents, as well as in those inactive solvents, such as acetone, which have no special heterolytic power for acidium and esterium ions. In marked contrast to mechanism A'1, the rates of reactions proceeding by mechanism A'2 depend on structure in such a way as to indicate (a) an inconsiderable electron demand at the seat of reaction, and (b) a high sensitivity to steric effects. This is well-established experimentally by the results of the classical researches of Victor Meyer, Kellas and Goldschmidt in the last century, and has been further extensively documented by the kinetic investigations of Sudborough, Palomaa, Skrabal, Hinshelwood, Hartman and others in more recent years.²⁹

The distinctive kinetic order of mechanism A'2 has been illustrated. It has long been common knowledge that the rate of hydrolysis of esters in water is proportional to the product of the concentrations of ester and of hydrogen ions. Proportionality to the water concentration could not, of course, be demonstrated so long as water was the solvent. However, it has recently been shown³⁰ that, in acetone as solvent, the rate is, indeed, proportional to the concentration of water, so that the complete expression for the rate of hydrolysis contains all the factors, $[H^+][Ester][H_2O]$, required by mechanism A'2. For esterification the demonstration is not so complete. The rate in alcoholic solvents is well known to be proportional to the product of the concentrations of the hydrogen ions and of the carboxylic acid. Using liquid acids, such as formic and acetic acid, as both solvent and reagent, Kailan has shown³¹ that the rate of the hydron-catalysed esterification of added alcohols varies with the alcohol. This proves some kind of dependence on the

²⁸ Unpublished investigation by J. Graham.

²⁹ Victor Meyer, *Ber.*, 1894, 27, 510; 1895, 28, 182, 1254, 2773, 3197; Victor Meyer and Sudborough, *ibid.*, 1894, 27, 1580, 3146; Goldschmidt, *ibid.*, 1895, 28, 3218; Kellas, *Z. physikal. Chem.*, 1897, 24, 221; Sudborough, *et al.*, *J. Chem. Soc.*, 1899, 75, 467; 1908, 93, 210; 1912, 101, 237; Kailan, *Annalen*, 1907, 351, 186; Drushel, *Amer. J. Sci.*, 1912, 34, 69; 1914, 37, 514; Palomaa *et al.*, *Ann. Acad. Sci. fenn.*, A, 1913, 4, 2; 1917, 10, 16; *Ber.*, 1935, 68, 303, 887; 1936, 69, 1338; 1938, 71, 480; McCombie and Scarborough, *J. Chem. Soc.*, 1915, 107, 156; Skrabal *et al.*, *Monatsh.*, 1924, 45, 141, and *loc. cit.*; Hinshelwood *et al.*, *J. Chem. Soc.*, 1935, 1588; 1938, 862, 1801. Hartman *et al.*, *J. Amer. Chem. Soc.*, 1937, 59, 2107; 1939, 61, 2167; 1940, 62, 1559.

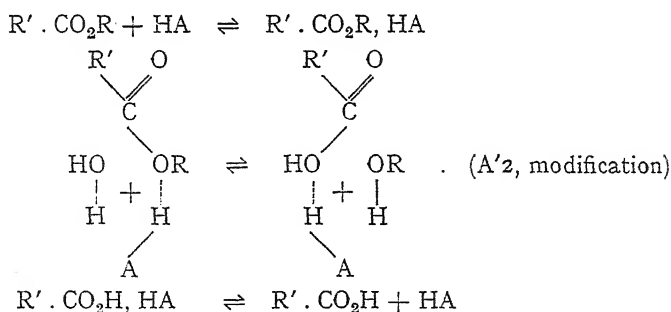
³⁰ Friedman and Elmore, *J. Amer. Chem. Soc.*, 1941, 63, 864. As has been shown in the example of substitution (Bateman, Cooper and Hughes, *J. Chem. Soc.*, 1940, 913; Church and Hughes, *ibid.*, p. 920), such a proportionality may sometimes arise from a medium effect alone; but this happens only in special circumstances, which do not apply in the present case.

³¹ Kailan and Brunner, *Monatsh.*, 1929, 51, 334; Kailan and Haas, *ibid.*, 1932, 60, 386; Kailan and Raff, *ibid.*, 1932, 61, 116; Kailan and Friedman, *ibid.*, 1933, 62, 284; Kailan and Alder, *ibid.*, 1933, 63, 155.

alcohol, but the results (contrary to a recent statement) are not sufficiently critical to establish the order with respect to alcohol.

One other kinetic criterion may be mentioned. The first step of mechanism A'2 (as also of A'1) consists of a preliminary reversible proton transfer. Now Bonhoeffer and Reitz have shown³² that, whilst the rates of aqueous reactions are usually reduced when ordinary solvent water is replaced by heavy water, this difference may become reversed in the case of reactions which proceed by a mechanism dependent on a pre-equilibrium involving a proton (or deuteron) transfer. Conversely they assumed that the observation of a larger rate in heavy water may be taken as an indication that the mechanism does involve such a pre-equilibrium. Roberts and Urey, having rejected mechanisms A'2 and A'1 in favour of the idea of rate-determining proton transfers,¹⁵ reject also Bonhoeffer and Reitz's criterion, because the acid-catalysed aqueous hydrolysis of carboxylic esters is one of the reactions which is known to proceed faster in heavy water than in ordinary water.³³ We assume mechanism A'2, which evidently brings Bonhoeffer and Reitz's rule and the observations into harmony.

As Hinshelwood has shown, esterification is catalysed, not only by hydrogen ions, but also, although much more feebly, by the undissociated molecules of the acid being esterified.³⁴ The demonstration of a similar catalysis by carboxylic acid molecules in ester hydrolysis is usually ascribed to Dawson and Lowson; but the effect they observed was very small, and its reality was only tentatively claimed by them.³⁵ The rate of self-catalysed esterification is proportional to the square of the concentration of acid molecules.³⁴ This is all that is positively established from an experimental and kinetic standpoint. Hypothetically we may suggest that the reaction involves, not a preliminary proton transfer, but rather the preliminary formation of a hydrogen-bond complex:



³² Bonhoeffer and Reitz, *Z. physikal. Chem.*, A, 1937, 179, 135; Bonhoeffer, *Trans. Faraday Soc.*, 1938, 34, 252; Reitz, *Z. Elektrochem.*, 1938, 44, 72.

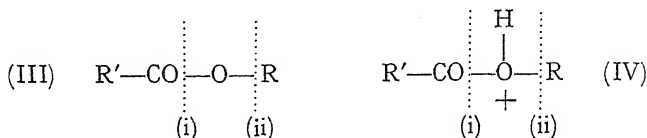
³³ Hornel and Butler, *J. Chem. Soc.*, 1936, 1361; Schwarz, *Z. Elektrochem.*, 1934, 40, 474.

³⁴ Rolfe and Hinshelwood, *Trans. Faraday Soc.*, 1934, 30, 935; Fairclough and Hinshelwood, *J. Chem. Soc.*, 1939, 593.

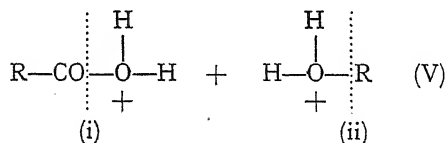
³⁵ Dawson and Lowson, *loc. cit.* Dawson Pycocock and Spivey (*loc. cit.*) established substantial catalysis with bisulphate ions, but it is not clear whether this catalysis is to be classed with those of acid molecules or with those of anions. The authors adopted the former view, but then Dawson, throughout his work on ester hydrolysis, assumed that he was dealing with general acid and basic catalysis, and this, as Hammett has pointed out (*Physical Organic Chemistry*, p. 256; McGraw-Hill, 1940), is at least not wholly true.

(5) Unimolecular and Bimolecular Acid Hydrolysis and Esterification with Alkyl-Oxygen Fission (A''1 and A''2).

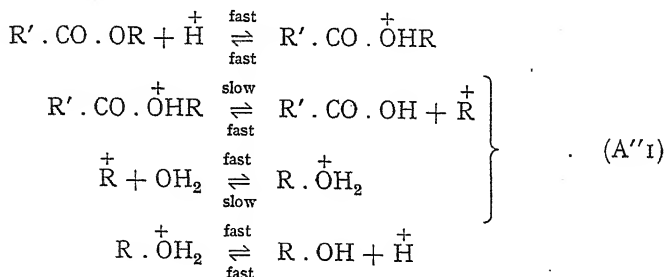
We shall be doing no violence to any of the considerations already presented if we suppose that an ester molecule has, in principle, a finite tendency to heterolytic fission at both (i) and (ii) in formula III, but that fission in position (ii) is so sensitive to the constitution of R that it can always be made to prevail by a suitable choice of structure. An extreme example is provided by the triarylcarbinyl esters, some of which, as Bowden has shown,³⁶ exist permanently ionised in position (ii).



In the esterium ion (IV), the positive oxonium charge must produce a considerably increased tendency to fission at both the positions (i) and (ii). We know empirically that in esters containing simple alkyl groups the favoured position is (i). We may again expect, however, that the tendency to heterolysis in position (ii) can be made to prevail by a suitable choice of the alkyl group R. The same is true for the pair of oxonium ions (V) derived from the system acid *plus* alcohol. The more usual position of heterolysis is at (i), but an appropriate form of R will render fission at (ii) the favoured mode. Our ability to realise this effect is guaranteed by the halochromism of triarylcarbinols, which shows that, under conditions in which the acidium ions derived from an acid such as acetic acid would undergo no heterolysis at (i), the oxonium ions of these alcohols are largely, or even completely, heterolysed at (ii):



These considerations establish the possibility of realising a unimolecular hydrion-catalysed hydrolysis and esterification, dependent on the separation of the alkyl group in the form of a carbonium ion as a sequel to a pre-equilibrium involving proton-addition:



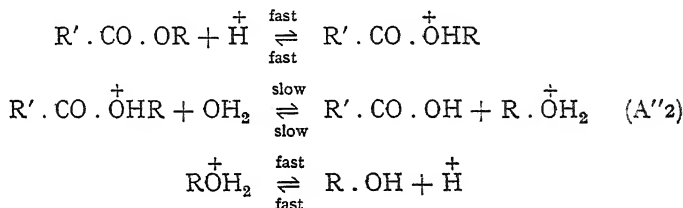
³⁶ Bowden, *J. Chem. Soc.*, 1939, 310; 1940, 874; cf. Ingold, *J. Soc. Chem. Ind.*, 1939, 58, 81.

Alkyl groups effective in promoting this mechanism should be found amongst secondary and tertiary structures, particularly those with α -aryl or other α -situated unsaturated substituents.

The characteristics of the mechanism are as follows. It is acid catalysed. It involves alkyl-oxygen fission, and the alkyl group, if asymmetric at the point of attachment, should be racemised. The initial rate of hydrolysis should be independent of water, and the initial rate of esterification independent of alcohol. Whilst demanding a strong electron release from R, the reaction should be but little sensitive to steric hindrance.

As we have noted, this mechanism is certainly realisable: it is probable that it has been under observation. In the esterification of optically active β -*n*-octyl alcohol with acetic acid, in this acid as solvent, and with sulphuric acid as catalyst, a considerable though partial racemisation was observed, which was shown to be dependent on the acid catalysis.²⁶ The result was explained by assuming the incursion of mechanism A''1. The confirmation of a more detailed investigation is obviously desirable.

We shall write down the complementary bimolecular mechanism, A''2, because it is conceivably observable, although we know of no evidence that its distinctive characteristics have been observed. For this reason its symbol is marked with a note of interrogation in Table I. It is derived by fusing together the two middle stages of the unimolecular mechanism into a single bimolecular process:



Its characteristics are as follows. It is acid catalysed. It involves alkyl-oxygen fission; and the configuration of an alkyl group which is asymmetric at the point of attachment should be inverted. The initial rate of hydrolysis should be of first order with respect to water, and the initial rate of esterification of first order with respect to alcohol. The reaction should require electron-releasing properties in the group R, and should be sensitive to steric hindrance.

(6) Summary of Mechanisms and Characteristics for their Diagnosis.

It is convenient to summarise the mechanisms of the hydrolysis and esterification in a comparative fashion. For simplicity we set out only the characteristic stages of the mechanisms, omitting, therefore, the final proton transfer in mechanisms of basic hydrolysis, and the initial uptake and final loss of proton in the mechanisms of acid hydrolysis and esterification. We also omit the variants of acid hydrolysis and esterification in which a whole (weak) acid molecule, instead of a proton, is "borrowed" by the system undergoing change. Mechanism A''2 has not yet been detected.

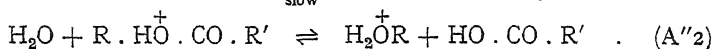
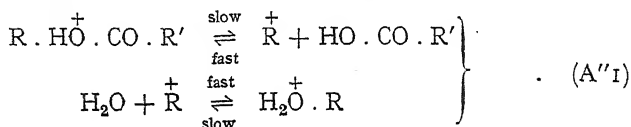
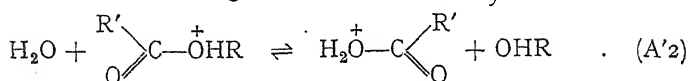
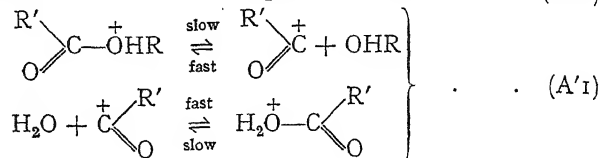
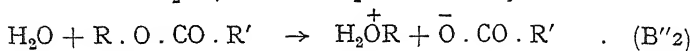
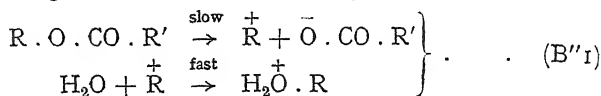
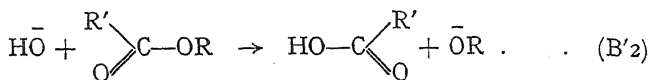


TABLE II.—DIAGNOSTIC CHARACTERISTICS OF MECHANISMS OF HYDROLYSIS AND ESTERIFICATION (FORMULATED AS FOR HYDROLYSIS).

Key.—Col. 3: Ac = acyl-oxygen fission; Alk = alkyl-oxygen fission.

Col. 4: Ret = retained; Rac = racemised; Inv = inverted.

Col. 5: E = ester.

Cols. 6 and 7: R and R' = groups in R'.CO.OR; (+) = electrons supplied by R or R'; (−) = electrons withdrawn by R or R'; a small sign-label indicates a small effect; (∼o) = a small effect the direction of which is not determined by theory.

Col. 8: × = sensitive; ○ = insensitive.

1. Mechanism.	2. Reagent (Hydrolysis).	3. Position of Fission.	4. Alkyl Configura- tion.	5. Kinetic Order (Hydr.).	6. 7. Electronic Requirements.		8. Steric Hindrance.
					R.	R'.	
B'_2	HO [−]	Ac	Ret	[HO [−]][E]	(−)	(−)	×
B''_1	H ₂ O	Alk	Rac	[E]*	(+)*	(−)*	○*
B''_2	"	"	Inv	[H ₂ O][E]*	(∼o)*	(−)*	×
A'_1	H ⁺ + H ₂ O	Ac	Ret	[H ⁺][E]	(∼o)	(+)	○
A'_2	"	"	"	[H ⁺][E][H ₂ O]	(∼o)	(∼o)	×
A''_1	"	Alk	Rac	[H ⁺][E]*	(+)*	(∼o)*	○*
A''_2 †	"	"	Inv	[H ⁺][E][H ₂ O]*	(+)*	(∼o)*	×

[* Not yet kinetically confirmed. † Mechanism not yet detected.]

Table II summarises the characteristics by which these mechanisms might be, and to a large extent have been, recognised. Those entries in the last four columns which are marked with an asterisk represent deductions from theory which have not yet been confirmed by kinetic observation, although we are pursuing the kinetic investigation of mechanisms $B''I$ and $A''I$ as well as of $A'I$.

We wish to thank Professor T. Campbell James for his continued hospitality.

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GENERAL DISCUSSION

Dr. R. P. Bell (*Oxford*) (*communicated*): In dealing with acid-catalysed esterification, Day and Ingold have supposed that catalysis by hydrogen ions involves a preliminary reversible proton transfer to the carboxylic acid, while in catalysis by acid molecules there is a reversible addition of these molecules by hydrogen bond formation. I should like to suggest that there may be a proton transfer in both cases, but that in the latter case this transfer constitutes the slow stage of the reaction. The carboxylic acid molecule has only weak basic properties, and in going from $R \cdot OH_2^+$ to $R \cdot COOH$ there is a very large decrease in acid strength (involving a factor of $10^8 - 10^{10}$) which may well reverse the relative rates of the two stages. As far as I know the evidence mentioned by Day and Ingold for the rapidity of proton exchanges between oxygen compounds refers only to cases where one of the reactants is a fairly strong acid or base. The velocity of exchange between two carboxylic acid molecules might be tested by experiments on hydrogen isotope exchange between two different carboxylic acids in an aprotic solvent.

Dr. Day and Prof. Ingold in reply (*communicated*): If, as Bell suggests in relation to catalysis by carboxylic acid molecules, the proton-uptake stage of mechanism $A'2$ is slow, and the subsequent attack by water or alcohol on the esterium or acidium ion is relatively fast, then the rate of hydrolysis will not contain the factor $[H_2O]$, and the rate of esterification will not contain the factor $[ROH]$. The presence of these factors has often been assumed for the acid-molecule-catalysed reaction, but never proved, so that no decision with regard to Bell's idea can at present be reached on these lines.

However, some indication can, we think, be obtained from a consideration of his proposed test for a slow hydrogen exchange between two carboxylic acid molecules. This experiment would not be particularly relevant to the problem if applied only to aprotic solvents, since the evidence advanced in favour of catalysis by acid molecules applies, for hydrolysis, to solvent water, and, for esterification, to methyl and ethyl alcohols as solvents. If, in such solvents, the observed rate of a proton-deuteron exchange between one carboxylic acid molecule and another approximately agreed with the measured rate of a closely related acid-molecule-catalysed hydrolysis or esterification, we should accept the result as strong evidence in favour of Bell's suggestion: conversely, his mechanism seems to require a result of this type. But an observed slow rate of hydrogen exchange would imply that the molecules of the solvent, the H_2O , $MeOH$, etc., would not operate as proton-carriers for a rapid proton transfer between one acid molecule and the other. This in turn would imply, either that the proton transfer from the acid molecule to the H_2O , $MeOH$, etc., is slow; or, that the proton transfer from the H_3O^+ ,
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MeOH_2^+ , etc., to the acid molecule is slow. We agree with Bell in rejecting the second alternative; which, moreover, in its application to hydrolysis and esterification does not accommodate the kinetic findings relating to the acid-molecule-catalysed reaction. Therefore we are thrown back on the first alternative, which, in plain language, says that the ordinary ionic dissociation of a carboxylic acid in H_2O , MeOH , etc., is slow. This is so contrary to one's preconceptions that we personally would not expect to find a slow hydrogen exchange between two carboxylic acids under the conditions in which, as it seems to us, the exchange ought to be slow if Bell's picture is to interpret recorded observations on the acid-molecule-catalysed process.

Dr. R. P. Bell, in reply (*communicated*): I agree that the points made by Day and Ingold render my suggested mechanism improbable, though not impossible. On the other hand, I do not think that their suggestion of an experimental test of hydrogen exchange between two carboxylic acids dissolved in water or an alcohol would decide the question, for in these solvents exchange could in any case take place by the irrelevant mechanism $\text{R}_1\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{R}_1\text{COO}^- + \text{H}_3\text{O}^+$ etc. In an aprotic solvent this type of exchange is, of course, absent.

Dr. C. L. Wilson (*Manchester*) said: In view of what has been said regarding the inception of the idea of ionisation in organic systems, the statement of Wislicenus in 1898 with reference to prototropic change is of some interest.¹ This writer remarked "It is impossible to pass over these phenomena without coming to the conclusion that the inter-conversion of isomers is connected with dissociation. Dissociation in these substances involves a loosening of the mobile hydrogen atom, undoubtedly as a cation. . . ."

With reference to the mechanism of hydrolysis, $\text{B}''1$, there is one very puzzling feature in optical resolution of alcohols, which might now find an explanation. It would seem to be true, without exception, that no tertiary alcohol has ever been resolved by the hydrogen phthalate method (Dr. Kenyon interpolated that this was so). We have seen, however, that a tertiary alkyl group has a strong tendency to separate as a cation under suitable conditions. If the alkyl group is optically active, ionisation of the phthalate would mean racemisation accompanied presumably by solvolysis. There could also be a special mechanism for racemisation in an optically active alkyl hydrogen phthalate involving inversion of the alkyl group through an attack by the other (ionised) carboxyl group ($\text{B}''2$ type): in this instance, however, the optical stability of secondary alkyl phthalates would require special explanation. These points may have some bearing on the recorded failures to resolve tertiary alcohols, and if this is so experimental support should be easy to obtain.

Dr. J. Kenyon (*London*) said: With reference to Wilson's suggestion that the known failure to resolve tertiary carbinols by recrystallisation of the alkaloidal salts of their hydrogen phthalates, might be due to racemisation of the phthalic ester, during its saponification, by the mechanism labelled $\text{B}''1$ by Day and Ingold,² or even to racemisation of the alkyl-phthalate ion, by a similar mechanism, during the recrystallisation or decomposition of its alkaloidal salt. From the practical standpoint, none of the phenomena associated with the separation of diastereoisomerides (*e.g.* changes in crystal habit, melting-point or solubility) had ever been observed during the attempted resolution of tertiary carbinols. Moreover, in known cases where racemisation occurred by the mechanism referred to, *e.g.* during the resolution of methylanisyl carbinol,³ the corresponding di-ester (di-methylanisyl carbinol phthalate) was formed as

¹ See Wilson, *Trans. Faraday Soc.*, 1938, 34, 176.

² *This volume*, p. 3B.

³ Balfe and Kenyon, *Nature*, 1941, 148, 196.

a by-product; no analogous observation had been made with the tertiary carbinols.

Dr. M. P. Balfe (*London*) said: On the same point, although the existence of this mechanism has been known for some years,^{2, 3, 4} it leads in the cases observed only to partial racemisation when sodium hydroxide is used for the saponification. To account for the complete racemisation of the esters of tertiary carbinols by this mechanism would therefore involve the improbable assumption that the tertiary carbinols whose resolution has been attempted have much more powerful electron-releasing properties than the carbinols to which the mechanism has been shown to apply.

Dr. Day and Prof. Ingold (*communicated*): With reference to Balfe's footnote,⁴ it is difficult to agree, in the absence of kinetic work, that mechanism B''I has been demonstrated; but it has been indicated, as we have already stated, in the work of Kenyon and his associates. If, however, we are to look for the first indications of this mechanism, it is necessary to go further back than 1936. In 1928 Burton and one of us⁵ proposed that allyl esters (the type handled by Kenyon) could ionise, that their rearrangements could be explained in this way, and that an anionoid group other than the original acyloxy-group could reappear after the change. If the new group is OH, this is hydrolysis; and in any case it is mechanism B''I. Kenyon, Partridge and Phillips acknowledged the origin in this work of the interpretation they gave to their own phenomena. Thus the matter did not, as would appear from Balfe's footnote, begin and end in 1936: it began some time before, and is not ended yet. It was pure forgetfulness that caused Hughes, Ingold and Masterman to overlook the whole of the past evidence when including mechanism B''I in their list of suggestions; and, as we have already mentioned, Balfe was one of those who drew our attention to the omission.

⁴ (*Communicated*): The mechanism which Day and Ingold label B''I, and describe as predicted in 1939 by Hughes, Ingold and Masterman (*J.C.S.*, 1939, 838), was demonstrated in 1936, and is specifically referred to in the second paragraph of the paper by Kenyon, Partridge and Phillips (*J.C.S.*, 1936, 85).

⁵ Burton and Ingold, *J. Chem. Soc.*, 1928, 904; Burton, *ibid.*, 1950.

MECHANISM OF THE ADDITION AND CONDENSATION REACTIONS OF CARBONYL COMPOUNDS.

By H. B. WATSON.

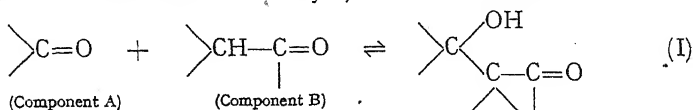
Received 8th September, 1941.

The literature dealing with these reactions is vast, and anything in the nature of a complete summary of the experimental work and theoretical considerations which have a bearing upon their mechanisms is quite impossible in the space of one short paper. Only a brief survey of certain aspects of the problems involved will therefore be attempted here.

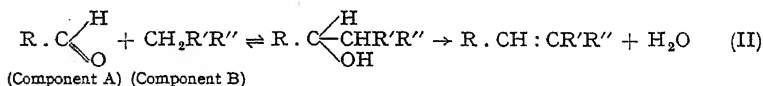
Whereas olefinic compounds, as a class, form addition products with electrophilic reagents such as halogens and halogen hydrides, the unsaturation of the carbonyl group is manifested in its power of adding nucleophilic reagents. The considerable dipole moments of ketones and aldehydes indicate a condition which may be written $\overset{\delta+}{\text{C}}=\overset{\delta-}{\text{O}}$, and the carbon atom of the group provides the point of attack for the nucleophilic reagent. This was demonstrated, for example, in the classic

work of Lapworth upon cyanohydrin formation; the effects of acids, alkalis and alkaline cyanides upon the addition of hydrocyanic acid to ketones could be interpreted satisfactorily only on the basis of a mechanism in which the first step is the co-ordination of cyanide ion at carbonyl carbon to give the complex anion $>\text{C}(\text{CN})\text{O}^-$, and this view of the reaction, which ascribes to cyanohydrins the characters of weak acids, was confirmed by the isolation of crystalline salts by the action of potassium cyanide upon benzaldehyde and upon camphorquinone.¹

The addition of a reagent of less powerful nucleophilic reactivity occurs under the influence of a catalyst, as in aldol condensations:



Component A is here an aldehyde, or sometimes a ketone, and component B is a molecule in which a neighbouring group has rendered a hydrogen labile or "incipiently ionised." The ease with which aldols lose the elements of water to produce olefinic compounds is well known, and it is generally accepted that the reactions associated with the names of Knoevenagel (aldehyde or ketone + malonic, acetoacetic or cyanoacetic ester or a nitro-compound, in presence of ammonia or an organic base) and Claisen* (aldehyde + aldehyde or ketone in presence of alkali) have an aldol addition as the first step; in certain cases the intermediate aldol has actually been isolated. The Perkin reaction falls into the same category; evidence recently summarised by Breslow and Hauser² (e.g., the possibility of replacing the salt by an inorganic or organic base) shows that the acid anhydride is here "Component B," in accordance with Perkin's original view. All these reactions are represented by suitable adaptations of the general scheme



They have recently been discussed by Hauser and Breslow,³ who refer to them collectively as reactions of the "Aldol type." Their occurrence is conditioned by the reactivity of Component A, the reactivity of the incipiently ionised hydrogen of Component B, and the effectiveness (usually the basic strength) of the catalyst. Thus, aldehydes always react as "Component A" more easily than ketones, and, whereas benzaldehyde condenses with malonic or acetoacetic ester in presence of ammonia, piperidine or other organic base, its reaction with acetophenone requires the more powerful hydroxide or alkoxide ion (i.e., for a given component A the ease of condensation follows the activity of the labile hydrogen of component B). Again, since the aldol stage is always reversible, and in certain cases the equilibrium may favour the initial reagents very strongly, the facility with which the aldol loses water may sometimes be a determining factor.

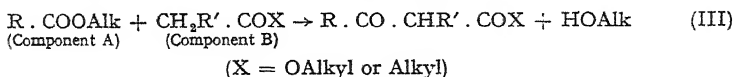
¹ Lapworth, *J.C.S.*, 1903, 83, 995; 1904, 85, 1206.

* The term "Claisen reaction" is applied both to this and to the acetoacetic ester condensation. In order to avoid confusion, the expression will be restricted hereafter to the latter.

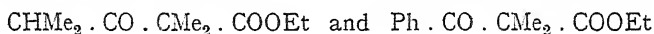
² *J. Amer. Chem. Soc.*, 1939, 61, 786.

³ *Ibid.*, 1940, 62, 2389, and references there cited.

Analogous to these changes is the Claisen acetoacetic ester synthesis. Component A is here an ester, anhydride or acyl chloride, and Component B is an ester or a ketone. A powerful base such as ethoxide ion is now necessary in view of the inferior reactivity both of Component A and of the hydrogen of Component B; in some cases, indeed, a still more powerful agent such as the triphenylmethyl anion is required. When the representation (III) is compared with (II),



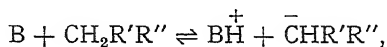
an important distinction between reactions of the Aldol and Claisen types becomes evident; in the latter, Component A possesses an anionic group which is eliminated with the hydrogen of Component B. While, for reasons given above, the production of an "aldol" is more difficult in (III) than in (II), its breakdown to form the ultimate product will be easier; the isolation of the "aldol" is therefore hardly to be expected, but its formation as an intermediate step may justifiably be assumed. In the best-known examples of the Claisen condensation, Component B has not less than two α -hydrogens, but this is not necessary; thus ethyl isobutyrate undergoes self-condensation and also condensation with ethyl benzoate in presence of sodium triphenylmethyl, giving



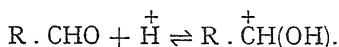
respectively.⁴

Although the catalysts most commonly employed are of the basic (electron-donating) type, there are examples of catalysis by acids (electron-acceptors), and Breslow and Hauser have now carried out a number of condensations in presence of the electron-accepting agents boron fluoride and aluminium chloride.⁵ These include the reaction of acetic anhydride with acetophenone (Claisen type), and of benzaldehyde with malonic ester (Knoevenagel) and with acetic anhydride (Perkin). Condensations of all the types dealt with above are therefore susceptible to the influence of both basic and acidic catalysts.

The mechanisms now usually accepted for reactions of the Aldol and Claisen types are essentially those put forward by Lapworth some forty years ago.⁶ They have been restated of recent years by Arndt and Eistert,⁷ by Hauser and co-workers,^{3, 4} and by others. Stated briefly, the view is that bases activate Component B by conversion to anion, *e.g.*



whereas acidic catalysts activate Component A by forming a co-ordination complex, *e.g.*,



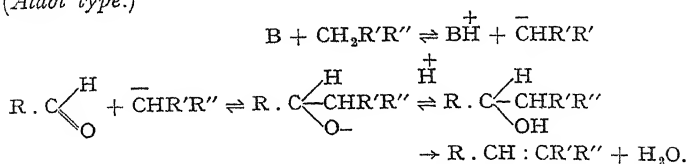
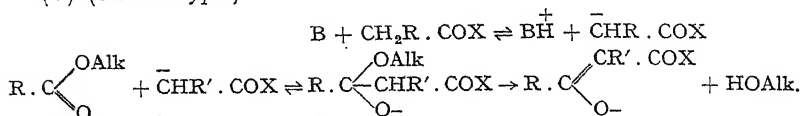
In the former case, the anion now adds to Component A, forming the ion of the aldol, and the complete schemes for reactions of the Aldol and Claisen types are represented by (IV) and (V).

⁴ Hauser and Renfrow, *J. Amer. Chem. Soc.*, 1937, **59**, 1823; 1938, **60**, 463.

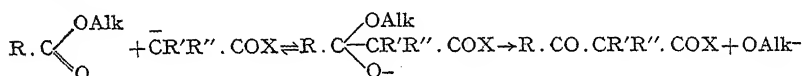
⁵ *Ibid.*, 1940, **62**, 2385.

⁶ Lapworth, *J.C.S.*, 1901, **79**, 1269; Hann and Lapworth, *ibid.*, 1904, **85**, 46.

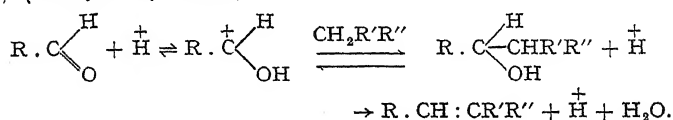
⁷ *Ber.*, 1936, **69**, 2381.

(IV) (*Aldol type.*)(V) (*Claisen type.*)

which, when only one α -hydrogen is present in Component B, would become



For catalysis by acids (*e.g.*, H^+ , BF_3) the mechanism is of the following nature (VI):

(VI) (*Catalysis by acids.*)

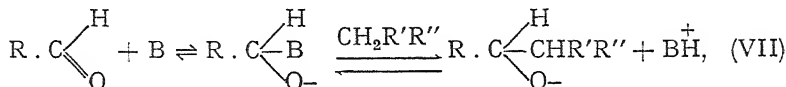
These schemes appear to be in harmony with most of the experimental observations. It may be supposed that, whereas the nucleophilic activity of Component B is not sufficiently great to enable it to attack the carbonyl carbon of Component A (as does the cyanide ion in cyanohydrin formation, for example), the anion of Component B can do this. In some cases the attack of the base may be the rate-determining step, the remaining stages being very rapid; this would account for the first-order kinetics of the conversion of acetaldehyde to aldol,* observed by Bell,⁸ who, however, suggests that the measurable reaction is the dehydration of a hydrated aldehyde molecule. On the other hand, a recent kinetic investigation of the condensation of benzaldehyde with acetophenone⁹ has shown that the speed is here proportional to the concentrations of both aldehyde and ketone, both of which must therefore be involved in the step which is measured. An acid catalyst must be regarded as rendering Component A sufficiently reactive to be attacked by Component B itself (instead of by its anion), and it may be deduced that a compound which is not sufficiently active to function as Component A even in presence of a base might do so under the influence of an acid catalyst; accordingly, Hauser and Breslow find that both diisopropyl ether and isopropyl alcohol condense with acetoacetic ester in presence of boron fluoride.³ There exists a whole multitude of facts, indeed, which are interpreted satisfactorily on the basis of these commonly accepted mechanisms.

* Compare Hammett, *Physical Organic Chemistry*, 1940, p. 343.

⁸ *J.C.S.*, 1937, 1637.

⁹ (Miss) Coombs and Evans, *ibid.*, 1940, 1295.

On the other hand, it is quite possible that a basic catalyst might initiate the reaction by an attack on the carbonyl carbon of Component A, just as cyanide ion adds in cyanohydrin formation, and as hydroxyl ion must add in the alkaline hydrolysis of an ester. Hammett¹⁰ points out, too, that a similar attack of a basic reagent upon carbonyl carbon occurs in the transformation of benzil to benzilic acid, in the addition of Grignard reagents to carbonyl compounds, and also, no doubt, in the hydroxyl-ion catalysed exchange of ¹⁸O for ¹⁶O in ketones,¹¹ while the reaction of carbon dioxide with hydroxyl or alkoxyl ion is a similar process.¹² The direct addition of ethoxide ion to Component A appears in the earlier mechanisms put forward to represent the Claisen condensation, and if reactions of the Aldol type proceed in this way they would be written as follows :



followed by the last two steps of scheme (IV). The distinction between mechanisms (IV) and (VII) may be purely academic, but it is interesting. It is obviously difficult to determine whether, in a base-catalysed condensation, the catalyst first removes a proton from Component B or whether it activates Component A by co-ordination at carbonyl carbon, for nearly the whole of the available data harmonise equally well with either scheme. Thus, the parallelism between the lability of the hydrogen of Component B and the ease of reaction remains, and a molecule such as that of diisopropyl ether or isopropyl alcohol has no point at which a basic catalyst could attack it.

A distinction might be attempted along the following lines, however. If the function of the catalyst is the removal of a proton from Component B, the energy of activation will be needed for this process and the anion will probably possess sufficient energy to bring about its reaction with Component A; constitutional changes in B will therefore be expected to have an important influence upon the measured value of *E*, whilst changes in A will not. If, on the other hand, the catalyst first co-ordinates with the carbonyl carbon of Component A to give a complex which possesses enough energy to react with Component B, the energy of activation will be needed for the formation of this complex, and will be influenced strongly by substituent groups introduced into A, but not by those introduced into B. This principle was applied in a recent investigation of the reaction of benzaldehyde with acetophenone in 90 % alcohol, to which reference has been made above.⁹ The results indicate that the introduction of groups into the aldehyde molecule leads to a distinct change in the energy of activation for its reaction with acetophenone; the values for benzaldehyde, anisaldehyde and *p*-chlorobenzaldehyde were 10,000, 11,000 and 8000 cal. respectively. But variations of the ketone molecule did not influence *E* to any great extent; with benzaldehyde as Component A, the values for acetophenone and its *p*-methoxy and *p*-chloro derivatives differed but little from 10,000 cal., changes in velocity being accounted for, presumably, by variations in the non-exponential term of the Arrhenius equation. It

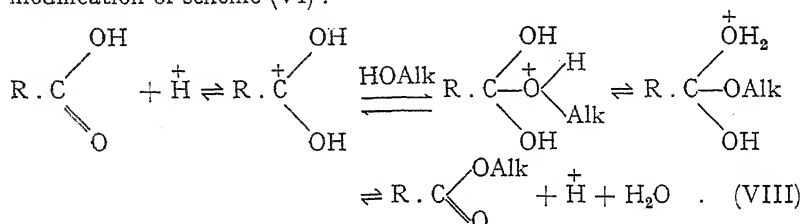
¹⁰ *Physical Organic Chemistry*, 1940, p. 329.

¹¹ Cohn and Urey, *J. Amer. Chem. Soc.*, 1938, **60**, 679.

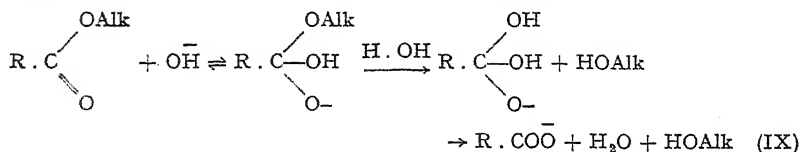
¹² Faurholt, *Z. physikal. Chem.*, 1927, **126**, 85.

would be quite unjustifiable, of course, to make sweeping generalisations from this single instance, but it is possible that an extension of work of this kind to other reactions may make it possible to draw more definite conclusions regarding the exact function of the basic catalyst. At the moment the Lapworth mechanism holds the field.

The reactions of carbonyl compounds with hydroxylamine and with hydrazines probably follow a course analogous to that of the condensations referred to here; oxime formation is accelerated by both acids and bases,¹³ although the semicarbazone reaction appears to be catalysed only by acids.¹⁴ Esterification and ester hydrolysis, which are dealt with elsewhere in this discussion, may also be brought into line with the general scheme. In esterification the acid is Component A and an alcohol molecule is Component B, and the following (VIII) is really a modification of scheme (VI) :



Incidentally, esterification, like the condensation reactions, is catalysed by boron fluoride.¹⁵ The acid hydrolysis of esters is, of course, the reverse of esterification, and alkaline hydrolysis may be represented by the necessary adaptation of scheme (VII) in which Component A is the ester and Component B a water molecule (a water molecule is usually regarded as necessary in alkaline hydrolysis, although it is not required in the equation);¹⁶ scheme (IX) may be suggested :



It is quite probable that a fundamental difference between the processes formulated in schemes (VIII) and (IX) is that, whereas in alkaline hydrolysis the energy of activation is used mainly in the linking of the hydroxyl ion, in esterification and acid hydrolysis only a small proportion of the energy is needed for the attachment of the acid catalyst, the greater part being employed in the binding of the alcohol or water molecule.¹⁷ Nothing is known concerning the energy of activation of acid-catalysed aldol condensations.

Finally, another process analogous to the condensations of carbonyl compounds is to be found in the addition of a nucleophilic reagent at a suitably activated olefinic linkage,¹⁸ as exemplified in reactions of the

¹³ Barrett and Lapworth, *J.C.S.*, 1908, 93, 85; Acree, *Amer. Chem. J.*, 1908, 39, 300.

¹⁴ Conant and Bartlett, *J. Amer. Chem. Soc.*, 1932, 54, 2881.

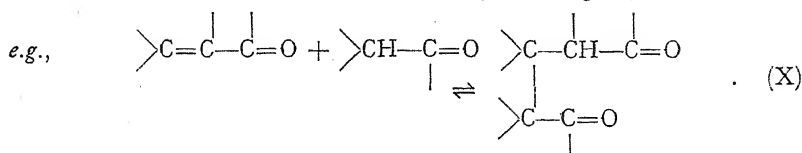
¹⁵ Nieuwland *et al.*, *ibid.*, 1932, 52, 2017; 1936, 58, 271.

¹⁶ Compare, for example, Newling and Hinshelwood, *J.C.S.*, 1936, 1357.

¹⁷ *Ann. Reports*, 1940, 37, 233, and refs. there cited.

¹⁸ Lapworth, *J.C.S.*, 1904, 85, 1214.

Michael type. The reactivity of the olefinic linkage with a compound containing incipiently ionised hydrogen is dependent upon the presence of a neighbouring group such as carbonyl, which renders the β -carbon atom susceptible to the attack of a nucleophilic reagent,



Certain reactions of this type have recently been studied by Hauser and co-workers,¹⁹ using sodium triphenylmethyl or sodium ethoxide as catalyst, and catalysis by boron fluoride and aluminium chloride has also been observed. The mechanism is doubtless quite comparable with that of the aldol condensation, as these workers suggest.

¹⁹ *J. Amer. Chem. Soc.*, 1940, **62**, 1763, 2385.

SOME OBSERVATIONS RELATING TO THE PROTOTROPIC CHANGES OF CARBONYL COMPOUNDS.

By H. B. WATSON.

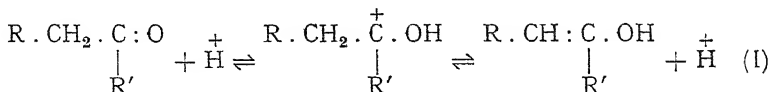
Received 8th September, 1941.

Various aspects of prototropic change were dealt with by speakers at the discussion on Reaction Kinetics held by this Society in September 1937, and it is obviously unnecessary and undesirable to traverse once again the ground there covered. The scope of the present paper will therefore be restricted to a few outstanding points of interest.

The prototropic changes of carbonyl compounds, like the condensations considered in the preceding paper, are accelerated both by bases and by acids, and therefore proceed by two distinct mechanisms; under the usual experimental conditions, the one or the other predominates according as the *pH* of the medium is higher or lower than that of the *isocatalytic* point. The "basic" and "acid" mechanisms proposed by Lapworth and Hann in 1902¹ are still accepted in their essentials, with the reservation that the same mesomeric anion is formed from either tautomeride. According to these schemes, the first step is either the removal of a proton by a base (basic mechanism) or the addition of a proton (acid mechanism). In either case, the formation of one tautomeride from the other involves, at a subsequent stage, the converse process, *viz.*, the addition of a proton in the basic mechanism or the removal of a proton in the acid mechanism.

Acid-Catalysed Prototropy.

This may be formulated as follows :



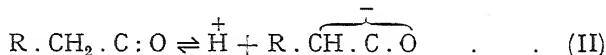
¹ *J.C.S.*, 1902, **81**, 1512.

The speed of the complete change is determined conveniently by Lapworth's halogenation method, and for optically active compounds having the α -carbon as the centre of asymmetry the rate of bromination is identical with that of acid-catalysed racemisation,² as would be expected. The co-ordination of the catalyst at carbonyl oxygen (in the ketonic form) is accompanied by a drift of electrons away from the α -hydrogen, which is thereby rendered more susceptible to the attack of a proton-acceptor (*e.g.*, in the medium). Three processes are involved, in fact, in the conversion of keto to enol in presence of an acid; (a) the linking of the acid catalyst at carbonyl oxygen; (b) the electromeric shift $>\text{C}=\ddot{\text{O}} \rightleftharpoons \text{C}=\ddot{\text{O}}^-$; and (c) the removal of the α -proton with the simultaneous movement of electrons to form the $\text{C}=\text{C}$ bond of the enol. If a polar substituent be introduced into one of the alkyl groups, it will influence (a) and (b) in the same sense (electron-attractive groups having an unfavourable effect and *vice versa*), and (c) in the opposite sense (electron-attractive groups facilitating the escape of the α -proton).

A kinetic investigation of the acid-catalysed prototropy of a series of nuclear-substituted acetophenones ($\text{R}=\text{H}$, $\text{R}'=\text{C}_6\text{H}_4\text{X}$) has shown that electron-attractive characters in X have an overall effect which is unfavourable to reaction, for they lead to lower velocities and higher energies of activation.³ Their predominant influence is upon processes (a) and (b), therefore, but the differences in velocities and energies of activation are small, on account of the opposite effect of the group upon process (c). Comparison may be made with the observed effects of groups upon the esterification of substituted benzoic acids, where the variations of the energy of activation are both small and irregular,⁴ and where again opposing factors are no doubt operative. Much larger differences are found in the condensations of substituted benzaldehydes with acetophenone⁵ and in the alkaline hydrolysis of benzoic esters,⁶ where opposing factors must be of far less importance. On the other hand, in the acid hydrolysis of benzoic esters, the unfavourable effect of an electron-attractive group upon the addition of the catalyst is outweighed by the facilitation, by the same group, of the co-ordination of a water molecule, and electron-attractive substituents lead actually to lower energies of activation just as they do in alkaline hydrolysis.⁷

Base-Catalysed Prototropy.

It is the commonly accepted view (see above) that the first step in the base-catalysed prototropy of a ketone is the transfer of an α -proton to the catalyst, a mesomeric anion being produced:



As Pedersen has pointed out,⁸ this view implies that there is no difference in principle between the acidic characters of a pseudo-acid (ketone,

² Wilson, *Trans. Faraday Soc.*, 1938, 34, 175.

³ Evans, Morgan and Watson, *J.C.S.*, 1935, 1167.

⁴ Hartman *et al.*, *J. Amer. Chem. Soc.*, 1937, 59, 2107; 1939, 61, 2167; 1940, 62, 1559.

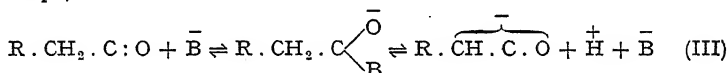
⁵ (Miss) Coombs and Evans, *J.C.S.*, 1940, 1295.

⁶ Ingold and Nathan, *ibid.*, 1936, 222; Evans, Gordon and Watson, *ibid.*, 1937, 1430.

⁷ Timm and Hinshelwood, *ibid.*, 1938, 862.

⁸ *J. Physical Chem.*, 1933, 37, 751.

nitro-compound) and of a true acid (enol, *isonitro*-compound), since both are genuine acids (proton-donors), although the former is much weaker than the latter. The mesomeric anion may justifiably be regarded as the entity which is halogenated at great speed, and the measured rate of bromination, deuterium exchange, or racemisation in a ketone where the α -carbon atom is asymmetric, which is found to be the same in the three cases within the limits of experimental uncertainty, may be equated with the speed at which this ion is produced.² In certain other prototropic systems (*e.g.*, methyleneazomethines) there is evidence that the anion never attains freedom, the removal of one proton and the addition of another (to give the tautomeride itself) being simultaneous; in keto-enol systems, however, the formation of the mesomeric ion is the controlling process, and, as Hammett points out, "there is no reason to suppose that the formation of an electrically neutral enol form represents anything more than an unimportant by-path into which a portion of the reacting substance may transiently stray. The necessary and sufficient condition for the halogenation, the racemisation, or the deuterium exchange is the formation of the ion."⁹ There is probably nothing inconsistent with the known facts, however, in the suggestion that the initial attack of a basic catalyst is upon carbonyl carbon rather than on hydrogen. This would imply that the primary process is analogous to cyanohydrin formation or to alkaline hydrolysis, whereas the usually accepted view seeks an analogy with the more powerfully acidic systems in which hydrogen linked to oxygen is ionisable. If the attack of the base is upon the carbonyl carbon, the mesomeric anion would be formed in two steps,



In either case the formation of the anion will be favoured by its energy of mesomerism.

Effects of Substituents upon Mechanism.

Since the presence of an electron-attractive group is unfavourable to prototropy *via* the acid mechanism, while it facilitates the transformation in the presence of a base, the effect of introducing such substituents will be to cause the change to proceed by the latter rather than by the former route. This has been found, for example, in the prototropy of ethyl pyruvate and of ethyl acetoacetate where the influence of an acid catalyst is small owing to the influence of the carbethoxyl group in the neighbourhood of the carbonyl group.¹⁰ When the electron-attractive group is removed further from the ketonic group (as in *lævulinic acid*),¹¹ its effect is much smaller, as would be anticipated. A more striking example is found in the observed effect upon the reaction mechanism of the progressive introduction of 1, 2, 3, and 4 bromine atoms.¹² When acetone is brominated in 50 % acetic acid medium, the addition of hydrogen chloride in increasing quantity leads to a consistently increasing velocity, but mono- and dibromo-acetones show a decreased speed when small

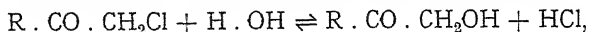
⁹ Hammett, *Physical Organic Chemistry*, 1940, p. 231.

¹⁰ Watson and Yates, *J.C.S.*, 1933, 220; Pedersen, *Trans. Faraday Soc.*, 1938, 34, 242.

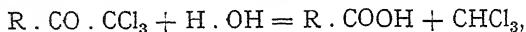
¹¹ Hughes and Watson, *J.C.S.*, 1929, 1945.

¹² Watson and Yates, *ibid.*, 1932, 1207.

quantities of mineral acid are present. Thus, for *s*-dibromoacetone the minimum velocity is reached when the added acid is at a concentration of 0.4 to 0.5 M, after which point a further increase of acidity leads to a greater speed; the basic mechanism clearly predominates in presence of acid not above 0.4-0.5 M concentration. The results for $\alpha\alpha\alpha$ -tribromo- and *as*-tetrabromo-acetone exemplify this feature in a remarkable degree; addition of halogen acid up to 2 M concentration (the highest employed in the experiments) leads to a continual decrease of speed, and hence reaction must proceed *via* the basic mechanism even in presence of these high acid concentrations. These highly halogenated ketones show other special features, such as the stability of their hydrates and other addition compounds. Further, whereas in dilute aqueous solutions mono- and di-chloroacetones exchange halogen for hydroxyl,



as-tetrabromo-, pentachloro-, and hexachloro-acetones under similar conditions undergo haloform cleavage,



this change occurring almost exclusively in the last-named.¹³ The presence of three halogen atoms linked to the same carbon is, of course, a necessity for the haloform cleavage, but, in addition, the electron-attractive characters of the halogen atoms confer upon the carbonyl carbon a high reactivity with nucleophilic agents (*e.g.*, OH⁻ ion), and subsequently the CX₃ group is eliminated similarly to the OR in an ester, the NR₂ in an amide, or the halogen in an acyl halide.

¹³ Edwards, Evans and Watson, *ibid.*, 1937, 1942.

GENERAL DISCUSSION *

Dr. H. B. Watson (Cardiff), before introducing the subject-matter of the two papers, said: As the senior member of the group of five pupils of the late Prof. Kennedy Orton, I should like to express our appreciation of the kind remarks made by Prof. Ingold † regarding our Professor and his work. We all acknowledge a deep debt to him, and it is a great joy to hear a tribute of this kind coming from one who was not actually a pupil of his.

Dr. R. P. Bell (Oxford) said: I should like to add one or two points to the paper by Watson on the addition reactions of carbonyl compounds. As he has mentioned, I have found that the aldol condensation of acetaldehyde in aqueous solution is of the first order with respect to the acetaldehyde, and had tentatively suggested that the rate-determining step might be the catalysed dehydration of CH₃CH(OH)₂. We have since obtained experimental evidence which disproves this suggestion. The species CH₃CH(OH)₂ would be much less volatile than CH₃CHO (*cf.* ethylene glycol), and if the equilibrium CH₃CH(OH)₂ \rightleftharpoons CH₃CHO + H₂O is not rapidly attained, then the rate at which acetaldehyde could be removed from solution by a stream of inert gas would be limited by the rate of the dehydration reaction. Actually we have found that this rate of removal can easily be made to exceed the velocity of the aldol condensation under the same conditions, thus showing that the latter cannot be governed by the velocity of dehydration. It may therefore be assumed that the slow reaction is the first order reaction with a base to give the

* On the two preceding papers by Dr. H. B. Watson.

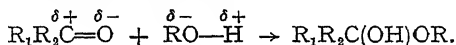
† See p. 602.

ion $\text{CH}_2^- \cdot \text{CHO}$, which then adds on rapidly to a second aldehyde molecule. This is in agreement with the observation of Bonhoeffer and Walters¹ that no deuterium becomes attached to carbon if the condensation is carried out in deuterium oxide: if the first step were reversible deuterium exchange on the carbon atom would be observed.

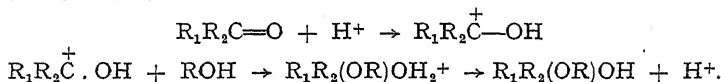
The dehydration hypothesis was originally suggested by the contrast between the aldol condensation of acetaldehyde and that of acetone, which does not form a hydrate to any appreciable extent. It is well known that the depolymerisation of diacetone-alcohol (catalysed by hydroxyl ions) follows first order kinetics, and this of course implies that the condensation is kinetically of the second order. This means that in the case of acetone the reaction with hydroxyl ion is reversible and fast, the slow stage being the reaction of the ion formed with a second acetone molecule. Confirmation is again obtained from work on deuterium exchange. The rate of aldolisation (calculated from the equilibrium constant and the de-aldolisation rate) is about one thousandth of the rate of deuterium exchange or of iodination under the same conditions.²

We have recently investigated the kinetics of the aldol condensation of isobutyraldehyde³ and find that the apparent order is intermediate between the first and the second, which indicates that in this case the two stages are probably of comparable rates. It would be interesting to know whether electronic theory can account for this change of kinetic behaviour in the series acetaldehyde, isobutyraldehyde, acetone.

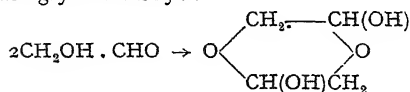
There is another class of addition reaction which can be included in the scheme given by Watson, namely *semi-acetal formation*, in which his component B is a hydroxy-compound. The reaction can be written



Catalysis by bases could be explained by the formation of the ion RO^- , which then adds on to the other component, while acid catalysis would follow the scheme



There is evidence that semi-acetals are formed in many cases when carbonyl compounds and alcohols are mixed, but few simple compounds of this class have been isolated (*e.g.* chloral alcoholate) and nothing is known of the kinetics involved. A special case of interest is when the hydroxyl compound is water: thus chloral hydrate is a well-defined compound, and there is much evidence for the formation of $\text{CH}_2\text{CH}(\text{OH})_2$ in aqueous solutions of acetaldehyde. It is of interest to note that the formation of the latter hydrate takes place at an observable rate and appears to be accelerated by hydroxyl ions.⁴ However, in spite of the paucity of information on simple semi-acetal reactions, ample confirmation of catalysis by acids and bases is available from other sources. Thus the ring formula for glucose contains the semi-acetal linking $-\text{O}-\text{CH}(\text{OH})-$, and the process of muta-rotation (well known as an example of acid-base catalysis) must involve the breaking and re-forming of this link. A similar but less familiar case is met with in the dimerisation of α -hydroxy-aldehydes and ketones, *e.g.* for glycollaldehyde



¹ Bonhoeffer and Walters, *Z. physikal. Chem.*, A, 1938, 181, 441.

² Walters and Bonhoeffer, *ibid.*, 182, 265.

³ Unpublished work by J. Neill.

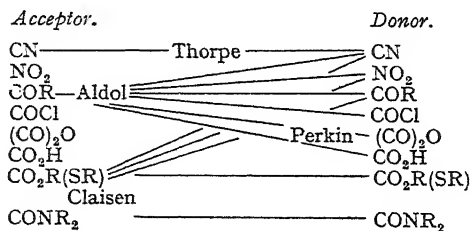
⁴ Perkin, *J. Chem. Soc.*, 1887, 61, 808; Brown and Pickering, *ibid.*, 1897, 81, 756.

The depolymerisation of the dimers of glycollaldehyde and of dihydroxyacetone has been shown to exhibit general acid-base catalysis in close analogy with the muta-rotation of glucose.⁵

Prof. C. K. Ingold (*London-Aberystwyth*) in regard to the paper on Carbonyl Compounds, said: In acid catalysis (equation VI) component A (represented as a carbonium ion) is evidently an electrophilic reagent. Component B should therefore be nucleophilic, a condition which is well satisfied if this component is an enol, but not if it is a ketone. A test of this conclusion is possible; for if component B is normally a ketone (as it frequently is), its enolisation will be a pre-requisite of reaction; and if, also, such an enolisation is rate-determining in aqueous acidic solvents (as it surely will be in certain cases), then the rate of reaction VII should be the same as the rate of bromination of component B under the same conditions.

(*Communicated*): Watson's suggestion that a basic catalyst acts, not as usually thought by extracting a proton from the methylene group of component B, but by adding on to the carbonyl group of component A (see his equation on VII), may be opposed on the following grounds. It seems axiomatic that any catalyst in any reaction must make one reagent more reactive towards the other. In the ordinary picture of the aldol reaction this task is accomplished by the basic catalyst when it converts component B (a carbonyl compound with a reactive methylene group) into its anion, the nucleophilic reactivity of which is obviously greater. In Watson's mechanism the attack of the base is on component A (a carbonyl compound), and would appear to be anticatalytic in nature for the following reason. The reactivity of component A is electrophilic, is centred in the carbonyl carbon atom, and is dependent on the unsaturation of the carbonyl group. A base does not increase this electrophilic reactivity if it satisfies it by offering its own unshared electrons for combination with the carbon atom, destroying carbonyl unsaturation in the process. I do not "catalyse" the efforts of a man to get his railway ticket if I push in front of him and get mine first, and then stay talking to the booking-clerk until he pushes me out of the way (*cf.* equation VII in which the characters of the parable can readily be identified). It is not suggested that this is anything more than a general argument,—too general to rank as demonstration.

Dr. C. L. Wilson (*Manchester*) said: There is one very simple consideration which would seem to outweigh all others in discrediting Watson's alternative schemes for carbonyl addition reactions (II) and



prototropy (III). In the latter, for instance, surely the loss of a proton by the simple carbonyl compound is going to be much easier than by the product formed by addition of a base, because co-ordination of the carbonyl group with a base will neutralise those polar factors which cause mobility of the α -hydrogen atom. Similar considerations apply to addition reactions. There is no real difficulty about the effect of substituents on the energy of activation of the reaction between benzaldehyde and aceto-

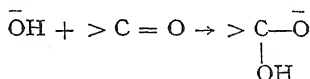
⁵ Bell and Baughan, *J. Chem. Soc.*, 1937, 1947; Bell and Hirst, *ibid.*, 1939, 1777.

phenone if it is remembered that the process involves two steps, (a) ionisation of acetophenone and (b) reaction of the ion with aldehyde. Either or both stages may control the reaction.

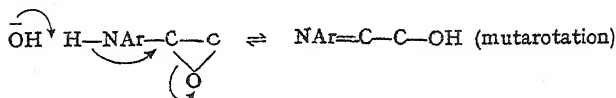
An alternative classification of reactants for carbonyl addition reactions may be found useful. This refers to component A as Acceptor and B as Donor; their functions are then immediately intelligible. Each of the various types of addition may then be represented by a tie line between two similar columns of activating groups as shown on opposite page.

For completeness it only remains to extend the donor group by inclusion of special types, such as fluorene and malonic ester.

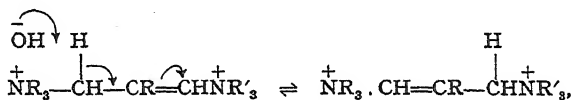
Dr. J. W. Baker (*Leeds*) (*Communicated*): The mechanism



for base-catalysed prototropy and carbonyl condensation reactions is favoured by Watson because of the correlation it effects with other carbonyl reactions. It would appear, however, that this argument applies even more strongly to the mechanism involving direct attack of the basic catalyst on the ionising hydrogen. The latter mechanism, equally satisfactory in the examples cited by Watson, is also applicable to the base-catalysed prototropy in systems of the type



and to triad systems activated only by positive poles, *e.g.*

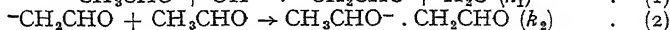


to which the co-ordination mechanism cannot be readily accommodated.

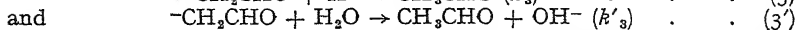
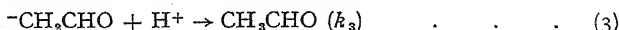
Dr. J. Weiss (*Newcastle-upon-Tyne*) (*Communicated*): In the formation of aldol from acetaldehyde the following two points must be taken into consideration:

- (a) The reaction is of first order with regard to acetaldehyde.⁶
- (b) No deuterium appears in the molecule (except in the OH group) if the reaction is carried out in heavy water.⁷

One is again led to the following simple mechanism which is already included in the general scheme of reactions given by Watson, *viz.* :—



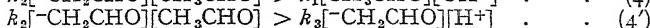
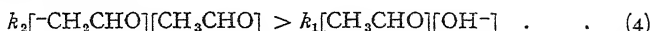
from (b) one must conclude that the recombination reactions:



are slow compared with reaction (2) under the experimental conditions in question.

At the same time reaction (1) must proceed more slowly than reaction (2) in order to satisfy (a).

We have the relations:



⁶ Bell, *J. Chem. Soc.*, 1937, 1637.

⁷ Bonhoeffer and Walters, *Z. physik. Chem.*, A, 1938, 181, 441.

This gives a possibility of estimating an upper limit for the electrolytic dissociation constant of acetaldehyde according to the reaction :



Combining equations (4) and (4') we obtain :

$$\frac{[^-\text{CH}_2\text{CHO}][\text{H}^+]}{[\text{CH}_3\text{CHO}]} < 10^{-16}$$

since k_1 can be taken from the work of Bell⁶ and k_2 (the rate constant of recombination of the ions) can be derived from Langevin's theory⁸ viz. : $k_2 = \frac{4\pi A}{D}$ where A is the conductance per molecule in e.s.u. and D the dielectric constant. As no mobility data are available for the ($^-\text{CH}_2\text{CHO}$) ion we have taken the value for the CH_3COO^- ion which seems to be a reasonable approximation. This gives a value of $k_2 \sim 4 \cdot 10^{13}$ (mol./l.)⁻¹ sec.⁻¹. This is an upper limit because mutual approach of the ions will not always lead to recombination, i.e. there may be a small heat of activation due to the molecular rearrangement taking place. A smaller value of k_2 would tend towards an increase of the dissociation constant. It seems reasonable to suppose that the actual value will be about 10^{-17} to 10^{-18} (at 25° C.).

Prof. C. K. Ingold (*Communicated*) : Watson has suggested that in the base-catalysed prototropy of a ketone the base adds to the carbonyl group (cf. equation III). This, it seems to me, would inhibit prototropy by neutralising the internal electron-attraction of the carbonyl group on which we believe the possibility of the proton separation to depend.

Dr. H. B. Watson (*Cardiff*) (*partly communicated*) : The addition of the basic catalyst to component A is admittedly hypothetical and highly controversial ; the only experimental evidence in its favour is found in the results published recently by Evans and Miss Coombs, which give good reason to believe that, when benzaldehyde reacts with acetophenone, substituents in component A (the aldehyde) influence the energy of activation while those in component B (acetophenone) do not. This would appear to indicate that the energy of activation is required (mainly, at least) for some process in which component A but not component B is concerned, and such a condition is fulfilled if addition of the catalyst to component A produces a complex having sufficient energy to enable it to react with component B. If, however, the catalyst first removes a proton from component B, energy must surely be required for this process, for it is hardly credible that a proton should be detached from acetophenone without energy of activation. Considerations of this kind give some plausibility to a mechanism in which component A is attacked by the catalyst. It might also be argued that, since addition of an anion at carbonyl carbon occurs in cyanohydrin formation, ester hydrolysis, etc., it is not impossible in the condensation reactions. For example, if ethyl acetate, under conditions leading to alkaline hydrolysis, first adds a hydroxyl ion, why should not the Claisen reaction be initiated by addition of ethoxyl ?

The mechanism of acid-catalysis set out in equation VI is not new. Excepting that the positive charge is usually written on the oxygen,

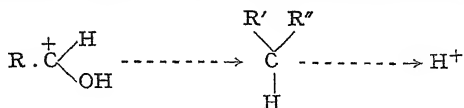
R. $\text{C} \begin{array}{c} \text{H} \\ + \\ \text{OH} \end{array}$, it is merely a restatement of commonly accepted views. The

complex R. $\text{C} \begin{array}{c} + \text{H} \\ \text{OH} \end{array}$ is admittedly electrophilic, but it seems not im-

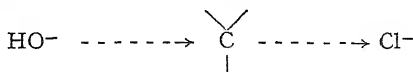
possible for it to react with $\text{CH}_2\text{R}'\text{R}''$ in the usual bimolecular manner,

⁸ Cf. Onsager, *J. Chem. Physics*, 1934, 2, 599.

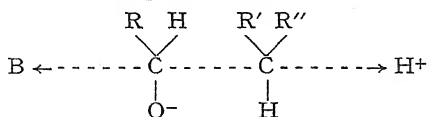
its approach being simultaneous with the withdrawal of a proton ;



This does not appear to differ in principle from



Base-catalysis, as set out in equation VII, would similarly be represented



and the driving force would be found in the energy possessed by the addition complex of the catalyst with component A.

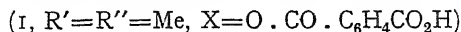
MECHANISM AND KINETICS OF ANIONOTROPIC CHANGE.

By M. P. BALFE AND J. KENYON.

Received 27th August, 1941.

In the course of an investigation on certain optically active α - and γ -substituted allyl alcohols and their derivatives, initiated with the object of throwing light on some unusual properties of $\alpha\gamma$ -dimethylallyl alcohol,¹ a number of observations have been made which have a bearing on anionotropic rearrangements. The kinetic studies in this work have been few in number, the speculations about mechanism being based almost entirely on stereochemical observations ; kinetic considerations are, however, necessarily implied by the suggested mechanisms. Kinetic studies by other workers in related fields² indicate that valid conclusions about the mechanism of reactions can frequently be drawn from stereochemical observations.

Before dealing with the experiments on anionotropy, it is desirable to refer to the results of replacement reactions with derivatives of the α - and γ -substituted allyl alcohols.³ Esters of these optically active alcohols, when heated with carboxylic acids or with alcohols, yield esters or ethers with extensive racemisation. The composition of the product of replacement reactions is controlled by the same factors as is the course of the anionotropic rearrangements which are described below. If the replacement reaction is stopped before it has gone to completion, the recovered portion of the original ester is often found to have undergone considerable racemisation. As an example, when the acid phthalic ester of optically pure (+)- $\alpha\gamma$ -dimethylallyl alcohol

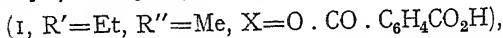


¹ Hills, Kenyon and Phillips, *Chem. and Ind.*, 1933, 52, 660; *J.C.S.*, 1936, 576.

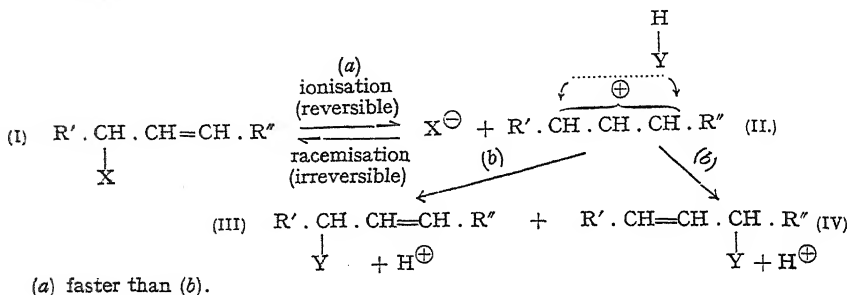
² Hughes, *Trans. Faraday Soc.*, 1938, 34, 202.

³ (a) Arcus and Kenyon, *J.C.S.*, 1938, 1912; (b) Balfe, Kenyon and Platt, *paper in course of preparation*.

is heated with acetic acid, the $\alpha\gamma$ -dimethylallyl acetate which is produced has only 0.8 % of the rotatory power of the optically pure acetate, while the recovered hydrogen phthalic ester is found to have undergone racemisation to the extent of 77 % (*i.e.* has 23 % of the rotatory power of the original phthalate). Similarly, the hydrogen phthalate of optically pure (+)- α -ethyl- γ -methylallyl alcohol



when warmed with methyl alcohol, yields an almost completely racemic hexenyl methyl ether (mixture of III and IV; $R' = Et, R'' = Me, X = OMe$).



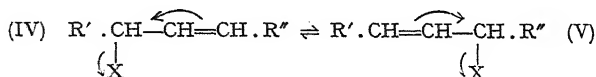
These phenomena are typical of the reactions which occur by intermediate ionisation of the reacting molecule into a carbonium kation and an anion, and which are therefore controlled by a first-order mechanism.² The ionisation, in stage (a) above, is facilitated by electron release from the double bond of the substituted allyl radical.

The chlorides of the substituted allyl alcohols undergo similar replacement reactions, with racemisation, for example in the hydrolysis of $\alpha\gamma$ -dimethylallyl chloride to $\alpha\gamma$ -dimethylallyl alcohol, a reaction which has been shown by Arcus and Smith⁴ to be of the first order.

The bearing of these observations on the theory of anionotropy is that they enable a distinction to be drawn between replacement reactions, which are accompanied by racemisation, and the rearrangements, which as described below occur with retention of configuration.

The results of the replacement reactions described above led to our making a general study of these reactions in esters of carbinols which contain electron-releasing groups, and we have found such reactions occur in these cases, by dissociation of the ester into a carbonium kation and an anion, to a greater extent than appears to have been previously realised.⁵

Our experiments on anionotropic rearrangements have dealt with the three-carbon system ($IV \rightleftharpoons V$) and, in general, the results have



confirmed two of the previously accepted principles.⁶ The rearrangement is promoted by electron-releasing α - and γ -substituent groups (R' and R'' in IV and V) in the allyl residue, and the product when equilibrium has been reached usually contains a preponderance of that

⁴ Arcus and Smith, *J.C.S.*, 1939, 1748.

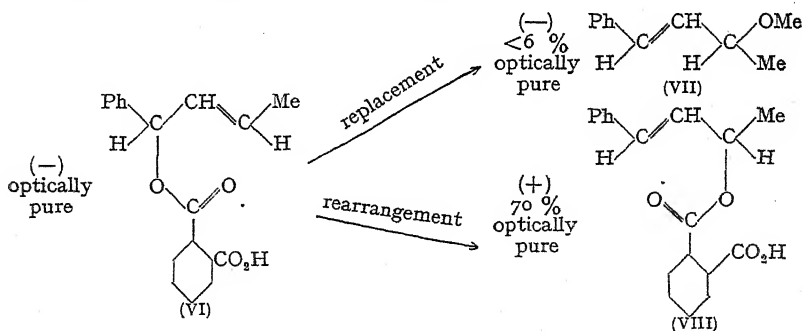
⁵ Balfe and Kenyon, *Nature*, 1941, 148, 196.

⁶ Baker, *Tautomerism*, London, 1934.

isomer in which the migrating radical is attached to the carbon atom of lower electron density. This is shown, for example, in the rearrangement of the hydrogen phthalate of α -phenyl- γ -methylallyl alcohol (VI \rightarrow VIII),⁷ and the rearrangement of the hydrogen phthalate of α -phenylallyl alcohol to that of γ -phenylallyl alcohol⁸: the latter rearrangement being less rapid than the former. We also confirm that the tendency of a group X to migrate is dependent on its anionic stability (*i.e.* the strength of the acid HX) though we have not made many experiments bearing directly on this aspect of the problem.

Kenyon, Partridge and Phillips made a somewhat extensive study⁷ of the anionotropic rearrangement of α -phenyl- γ -methylallyl hydrogen phthalate which they showed to be kinetically unimolecular in carbon disulphide solution. The rearrangement takes place both in the solid state and in solution in a variety of solvents: it is accelerated by rise in temperature, becoming instantaneous in benzene solution at 55–60° C. The change is accompanied by a high degree of retention of optical activity; optically pure (–)- α -phenyl- γ -methylallyl hydrogen phthalate, in the homogeneous state, rearranges into (–) + *dl*- γ -phenyl- α -methylallyl hydrogen phthalate which has approximately 70 % of its maximum rotatory power; the greatest retention of optical activity observed when the reaction occurs in solution is 58 % (in carbon disulphide solution).

This retention of asymmetry during the rearrangement is in marked contrast to the extensive racemisation which occurs during replacement reactions of the hydrogen phthalic ester. Furthermore, the small proportion of optical activity retained during the replacement reactions is derived from a product possessing the opposite configuration as well as opposite sign of rotatory power, to the product of the rearrangement. These observations, summarised below, indicate a fundamental difference in mechanism between the two reactions.



The argument that the rearrangement involves complete ionic dissociation,⁹ because in the presence of acetate ions α -phenyl-allyl *p*-nitrobenzoate yields cinnamyl acetate and not cinamyl *p*-nitrobenzoate, is thus shown to be invalid, because this reaction is a replacement and not a rearrangement.

In cases of molecular rearrangement where the migrating group is optically active, it is established that retention of asymmetry during

⁷ Kenyon, Partridge and Phillips, *J.C.S.*, 1939, 1697.

⁸ Duveen and Kenyon, *ibid.*

⁹ Burton, *ibid.*, 1928, 1650; 1929, 455.

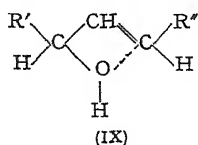
the rearrangement is evidence of its intramolecular nature.¹⁰ Although the anionotropic rearrangement is a different case (the asymmetric atom in the product of the rearrangement is not that which is asymmetric in the original compound), it is reasonable to apply the same conclusion, since the fixation, by the double bond, of the relative positions of the phthalate radical and the γ -methyl group in α -phenyl- γ -methylallyl hydrogen phthalate (which probably has the *trans*-configuration),¹¹ and the spatial proximity of the doubly bonded oxygen atom to the γ -carbon atom (illustrated in formula VI), hold the phthalate radical in such a position that formation of a preponderance of one of the two possible configurations of the γ -phenyl- α -methylallyl derivative is facilitated. It is to be noted that in this hypothesis, a six-membered pseudo-cyclic configuration, rather than a four-membered structure⁷ is suggested; this point is referred to below.

Recently we have completed an examination of the rearrangement of α -ethyl- γ -methylallyl alcohol into α -methyl- γ -ethylallyl alcohol.¹² It has been found that optically pure (+)- α -ethyl- γ -methylallyl alcohol after standing in the homogeneous state for three years, is converted to a mixture of (+)- α -ethyl- γ -methylallyl alcohol (41 %), (+)- α -methyl- γ -ethylallyl alcohol (32 %) and *dl*-material (27 %). The rotatory power falls during this period from $\alpha_{5461}^{20} + 5.95^\circ$ to $\alpha_{5461}^{20} + 4.06^\circ$ (*l*, 0.25), most of the decrease occurring between the twenty-fifth and the four-hundredth day.

Now, if the rearrangement were irreversible, there would be a steady fall in optical rotatory power, whereas in fact there is, during the initial twenty-five days, a slight rise (to $\alpha_{5461}^{20} + 6.14^\circ$), due presumably to the formation of (+)- α -methyl- γ -ethylallyl alcohol. It is therefore more probable that the process is reversible, both isomers being formed with some racemisation. In the light of the figures just quoted, this conclusion indicates that there is a high probability that the rearrangement of any one molecule will occur with the retention of optical activity, from which it may be deduced that the rearrangement is intramolecular. Further light would be thrown on this question by an examination of the composition of the product at various stages during the rearrangement, but this we have not as yet been able to undertake.

Anomalies in the parachors of allyl alcohol and the α - and γ -substituted allyl alcohols indicate some peculiarity of structure. We suggest that in these alcohols there is some form of co-ordination between the hydroxyl group and the γ -carbon atom (IX) since this suggestion is in harmony with the considerable retention of optical activity during the rearrangement.¹² The carboxylic esters of these alcohols, on the other hand, do not exhibit any systematic parachor anomalies, and the six-membered pseudo-cyclic formulation brings the atoms into suitable positions for rearrangement with retention of optical activity, without the necessity for assuming any further peculiarities of structure.

The conclusion that the rearrangement of α -ethyl- γ -methylallyl alcohol leads to a condition of dynamic equilibrium is in harmony with previous views.⁶ The chemical and optical stability of γ -phenyl- α -



¹⁰ See references quoted by Kenyon and Young, *J.C.S.*, 1941, 263.

¹¹ Arcus and Kenyon, *ibid.*, 1938, 312.

¹² Ains, Balfe and Kenyon (*in preparation*).

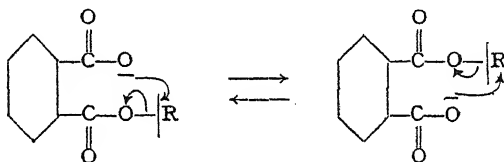
methylallyl hydrogen phthalate (VIII)¹³, when compared with the rapid rearrangement of its isomer (VI \rightarrow VII), indicates that when the electron-releasing powers of the α - and γ -substituents are very dissimilar, the reverse reaction (VIII \rightarrow VI) must take place so slowly as to be negligible.

¹³ Kenyon, Partridge and Phillips, *J.C.S.*, 1936, 85.

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GENERAL DISCUSSION

Dr. E. D. Hughes said: The racemisation observed in the reactions of certain optically active esters may be due to the operation of an internal mechanism in which the group R is transferred from one oxygen atom to another, *e.g.*,



The suggested reaction is a one-stage substitution and the transfer of R will be accompanied by inversion. In the example considered the reaction will be symmetrically reversible, and, given sufficient opportunity, the ester would be completely racemised. In the presence of extraneous reagents, however, a replacement reaction may intervene. The activity of the product will then depend on the mechanism of the replacement, and on the relative rates of the replacement and radical-migration processes, which, in turn, will depend, *inter alia*, on the nature of the group R. Recent work has shown that reaction mechanism is intimately dependent on the structure of the reactants and the conditions of reaction, and it should be emphasised that the above scheme is not intended as a complete alternative to the mechanism, involving the separation of a carbonium ion, adopted by Balfe and Kenyon in the interpretation of their results. It is suggested that some of the observations can be explained more satisfactorily on the basis of the mechanism herein outlined, but further experiments (particularly kinetic experiments) are needed in order to establish the range of application of either viewpoint.

Dr. J. T. Hewitt (*Hurst, near Reading*) said: If, in an acid phthalic ester, a tertiary alkyl radical is ionised and cannot be assigned to either of the carboxyl groups exclusively, then the failure to resolve alcohols of the type $\text{CR}^1\text{R}^2\text{R}^3\text{OH}$ by conversion into acid phthalic esters and fractional crystallisation of the salts of the latter with optically active bases is understandable. Since the method effects the resolution of secondary alcohols, is one to understand that in the acid esters of such alcohols, the secondary alkyl group can be definitely assigned to one carboxyl group?

Dr. Hughes said: The applicability of the radical-migration mechanism of racemisation will depend on the nature of the group R (*cf.* above), and the observations indicate that it is relatively unimportant in the case of the secondary alkyl groups.

Dr. M. P. Balfe, in reply, considered that Hughes' suggestion complicated, without improving, the original formulation, and therefore considered that it should only be accepted if the evidence made it essential.

(*Communicated*): In general, the racemisation of the reaction product which is observed during reactions of the alkylphthalate anion (*e.g.* in

Scheffer showed that the relative rates of further nitration at the different positions in mono- and di-substituted benzene derivatives could be reproduced with satisfactory accuracy by assuming that the difference in substitution entropy is zero for the different hydrogen atoms, that is, the relative velocities of formation of isomerides depend only on an energy difference, a result of considerable significance. The calculation, moreover, is of interest as, we believe, the first instance of the interpretation of the relative velocities of organic reactions in solution in terms of the parameters of the Arrhenius equation.

Without being aware of Scheffer's previous work, Bradfield and Jones¹² repeated the analysis of Holleman's data in terms of the Arrhenius equation, interpreting the constants, however, in the light of the theory of kinetic activation, then being successfully applied to gaseous reactions. The constant B appears as PSZ , where Z is the collision number, P denotes the probability that phase conditions are favourable to reaction, and S is a factor depending on the shape of the molecule, representing the probability that orientation of the reacting molecules is appropriate.* It is important to note that the calculation is independent of the actual mechanism of the reaction. The substituting agent may be the nitric acid molecule or any other nitrating agent, formed by any series of reactions, fast or slow. The reagents may be mixed slowly or rapidly, the exact experimental procedure is immaterial so long as (1) the temperature is maintained constant, (2) the side reactions are of the same order, and (3) the nitration takes place in a single phase. That this last condition may sometimes be essentially satisfied even when the reaction mixture is not homogeneous, is indicated by the proof that in the nitration of nitrobenzene by $H_2SO_4-HNO_3$ under non-homogeneous conditions, the reaction takes place mainly in the acid layer, the velocity in the organic layer being very small.¹³

For the further elucidation of the mechanism of nitration, complementary information is required concerning the actual rates of substitution in different molecules. A summary, with literature citations, of attempts to obtain such information has recently been given by Benford and Ingold,¹⁴ from which it is clear that:—

(1) Nitration of benzene and many of its derivatives in sulphuric acid is too fast for measurement. For certain derivatives containing one or more strongly deactivating nitro-groups, a straightforward second order constant is observed.

(2) Nitration of benzene and its derivatives in acetic anhydride solution is catalysed by nitrous acid, and is complicated by interaction between the solvent and the nitrating agent.

(3) The nitration of phenol in water and other solvents is catalysed by nitrous acid.

Employing a dilatometric method, Benford and Ingold made a detailed study of the nitration of benzene, toluene, ethylbenzene and the four halogenobenzenes in nitromethane. They found that the nitration of benzene and the two alkyl benzenes proceeds as a reaction of zero order with respect to the substance nitrated. The reaction is

¹² *J.C.S.*, 1928, 1006.

* The factors of the temperature independent term PS cannot be separated by experiment. It is usual now to indicate this composite term by P . Bradfield and Jones wrote PS merely as a reminder that the factor is not simple.

¹³ Hetherington and Masson, *J.C.S.*, 1933, 105.

¹⁴ *Ibid.*, 1938, 929.

retarded by nitrous acid in accordance with the law: $k_0 = 1/(a + b\sqrt{n})$, where n is the concentration of nitrous acid and a and b are functions of the nitric acid concentration. At the lowest attainable concentration of nitrous acid the reaction remains of zero order. Under precisely similar conditions the reaction proceeds at the same rate for all three hydrocarbons. With fluoro- and iodobenzene, and still more with chloro- and bromobenzene, the reaction rates show signs of dependence on the concentration of the aromatic substance, this dependence being more marked as the reaction proceeds. These facts indicate that, as a minimum, two successive stages must be considered, the first reaction or reactions, relatively slow, not involving the aromatic compound. With the halogenobenzenes, the second stage, the actual nitration, is sufficiently slow to have some effect on the over-all velocity. From a detailed consideration of the relevant facts, Benford and Ingold put forward a scheme in which the effective nitrating agent is considered to be $\text{CH}_2 : \text{NO} \cdot \text{ONO}_2$, formed by isomerisation of the nitromethane used as solvent, followed by condensation with nitric acid. Nitrous acid (or the "nitrous reagent"), it is suggested, retards the reaction by interaction with $\text{CH}_2 : \text{NOOH}$. It is obvious that the activation energy for any reaction in which the aromatic compound is directly concerned cannot be deduced from a study of the effect of temperature.

In a survey of nitration solvents it is shown that they may be divided into three groups. In the first are dioxan, acetic acid and acetonitrile, in which nitration proceeds slowly, the effective nitrating agent being probably the nitric acid molecule $\text{HO} \cdot \text{NO}_2$. Nitromethane and acetic anhydride are solvents of intermediate type, in which the nitric acid becomes acylated to yield the stronger nitrating agent AcONO_2 . Sulphuric acid is a fast solvent, where almost certainly $\text{SO}_3\text{H} \cdot \text{NO}_2$ is the active agent. It is suggested that in nearly absolute nitric acid, and possibly in mixed acid, the cation $\text{NO}_2 \cdot \text{OH}_2^+$ (a tautomer of the cation shown to exist by Hantzsch¹⁵) is the nitrating agent.

Returning to the question of the rates of nitration, there remains the competition method of determining relative velocities. In spite of considerable experimental difficulties, this method has been successfully applied to a determination of the relative rates of nitration in acetic anhydride (presumably by acetyl nitrate) of benzene, toluene,¹⁶ ethyl benzoate,¹⁷ and the halogenobenzenes.¹⁸ By combining the figures for the total velocity of nitration of a mono-substituted compound relative to benzene with the proportions of isomerides formed, figures are derived for the partial rate factors, *i.e.*, the factors by which the orienting substituent changes the specific rates of substitution in the individual nuclear positions. In this method of attack, the almost insuperable difficulties offered by a direct kinetic approach are outflanked. For, as Ingold and Smith say, provided the reactions proceed homogeneously, "the only essential assumption is that the attack of the nitrating entity (whatever that may be) on the aromatic compound is unimolecular with respect to the aromatic compound. Nothing else matters: the active agent may be unknown and its attack of any total order; it may be produced in some preliminary change—possibly slow, possibly reversible:

¹⁵ *Ber.*, 1925, 58, 941.

¹⁶ Ingold, Lapworth, Rothstein and Ward, *J.C.S.*, 1931, 1959.

¹⁷ Ingold and Smith, *ibid.*, 1938, 905.

¹⁸ Bird and Ingold, *ibid.*, 1938, 918.

it or some material essential to it, may be simultaneously concerned in a dozen independent or mutually interdependent side reactions . . . yet the competition method will give the right result." ¹⁷

The so-obtained partial rate factors for the several positions available in the substances examined are shown in Table I. It is noteworthy

TABLE I.

	<i>Ortho.</i>	<i>Meta.</i>	<i>Para.</i>
Benzene . . .	1	1	1
Toluene . . .	43	3.0	55
Ethyl benzoate	0.0026	0.0079	0.0009
Chlorobenzene .	0.030	0.000	0.139
Bromobenzene .	0.037	0.000	0.106

that whereas *ortho-para* substitution of toluene results from activation of all positions, the *meta* position being least activated, the *ortho-para* direction of halogen is the result of deactivation of the *meta* position more strongly than the *ortho-*

para positions. For ethyl benzoate, the opposite kind of deactivation leads to *meta* substitution. This result is entirely in accord with the qualitative expectation of the electronic theory of reactions.

Of considerable significance also is the effect of conditions on the partial rate factors for chloro- and bromobenzene, which has been studied in some detail. For nitration in acetic anhydride, acetonitrile and nitromethane, the variations in F (the partial rate factors) are small and not very regular. The change in F over the temperature range 0° - 35° is considerable, and is generally greater for the smaller partial rate factors than for the larger ones. Since F is a ratio of velocities, the variation in F with temperature may be examined with the aid of an expression of the type of Equation (1). If it be assumed that the orienting substituent in chloro- and bromobenzene affects the rate of reaction by changing *only* the energy of activation at the several nuclear positions, the entropy term becomes zero, and it will be seen that $-T \log F$ should be independent of temperature. Bird and Ingold ¹⁸ tabulate values of $-T \log F$ for the nitration of the two halogenobenzenes in the solvents named above. From their figures it may be seen that while between 0° and 35° the absolute temperature varies over a range of 13 %, the average variation of $-T \log F$ between the same two temperatures is only 2.5 %. The authors consider that this latter variation exceeds the experimental error in the determination of F , nevertheless, there can be no doubt that most of the change in T is compensated by an opposite change in $-\log F$. This nearly complete compensation means that nearly the whole effect of the substituent is concerned with the energy of substitution in the several nuclear positions. The relation between the effect of these substituents on the activation energy for nitration and their effect on the activation energy in other reactions is discussed on page 741.

Regarding the proportions of isomerides formed in nitration, it is of interest that Ri and Eyring ^{18a} have recently succeeded in calculating from dipole moment data the amounts of isomerides formed in the nitration of nitro-, chloro-, bromo- and iodobenzenes. By making certain reasonable assumptions, the charge, ϵ_y , at a reacting carbon atom of a monosubstituted benzene derivative resulting from both inductive and mesomeric polarisation is deduced. The charge distribution

is connected with the rate of nitration by assuming that the electrostatic interaction between the reacting carbon atom and NO_2^+ (considered as the essential nitrating entity) changes the activation free energy ΔF for the nitration of benzene by an amount $\epsilon_y \epsilon_n / (rD)$, where ϵ_n is the charge on the NO_2^+ ; r , the distance between, and D , the dielectric constant of the medium between the NO_2^+ and the carbon atom, are taken as 1.6 Å. and unity, respectively. Hence for the rate of reaction at a given carbon atom:

$$\ln k_y = [\Delta F + \epsilon_y \epsilon_n / (rD)] / RT + \text{const.}$$

The relative rates of nitration at the *ortho*, *meta* and *para* positions calculated by combining expressions of this type are in reasonably good agreement with the experimental data.

Sulphonation.

When a mono-substituted benzene derivative is sulphonated, the relative rates of substitution at different positions are not always derivable from the amounts of the isomerides isolated, as it has long been known that in certain cases migration of the sulphonic acid group takes place following the substitution reaction.¹⁰ The mechanism of this migration is uncertain. However, when *o*- or *p*-toluene sulphonic acid is heated with sulphuric acid at 100°, an equilibrium: *ortho* \rightleftharpoons *para* is reached, while no *m*-sulphonic acid is formed. Since, on the one hand, some *m*-sulphonic acid is formed in direct sulphonation of toluene, and on the other, the *m*-compound is unaltered by treatment with sulphuric acid at 100°, Holleman and Caland¹⁹ conclude that the migration of the sulphonic acid group between the *ortho* and *para* positions is not accounted for by assuming hydrolysis followed by re-sulphonation of the toluene. However, despite the complexity introduced by possible migration, some progress has been made in the analysis of the kinetics and mechanism of sulphonation.

It was found by Martinsen²⁰ that the constants calculated for the sulphonation of *p*-nitrotoluene on the basis of a bimolecular reaction with sulphuric acid fell as the reaction progressed. Joffe²¹ made certain corrections to these results and endeavoured to explain them by assuming that the sulphuric acid acted as an acid catalyst and the cause of a back reaction. Comparative determinations of the rates of sulphonation of some phenols have been made by Campbell.²²

An investigation of the sulphonation of nitrobenzene by sulphur trioxide dissolved in excess of nitrobenzene has recently been reported by Vicary and Hinshelwood.²³ This reaction, which is of the second order with respect to the sulphur trioxide, undergoes a marked retardation when about 50 % of the sulphur trioxide has reacted. If it be assumed that the sulphonic acid forms a complex with the sulphur trioxide, and that only the fraction α of the sulphur trioxide remaining free is active for sulphonation, then $dx/dt = k\alpha^2(a-x)^2$ and

$$\alpha = \text{const.} \sqrt{(dx/dt)/(a-x)^2}.$$

Values of $\Delta x/\Delta t$ from the reaction-time curves are substituted in this

¹⁹ *Ber.*, 1911, 44, 2504.

²⁰ *Z. physikal. Chem.*, 1908, 62, 713.

²¹ *J. Gen. Chem. Russia*, 1933, 3, 437, 505.

²² *J.C.S.*, 1922, 847.

²³ *Ibid.*, 1939, 1372.

expression, and as $\alpha = 1$ when $x = 0$, values of α for different values of x are obtained. It is found that the equilibrium constant

$$K = [\text{complex}]/[\text{SO}_3][\text{sulphonic acid}]$$

calculated from the value of α for $x = 50\%$ enables values of α to be calculated for the whole course of the reaction in fair agreement with experiment. Velocity constants are calculated from the expression $k = (\Delta x/\Delta t)/(a-x)^2\alpha^2$.

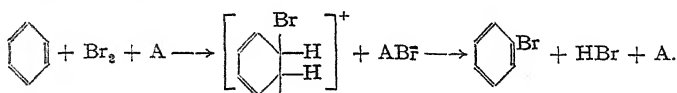
The molecular complexity of sulphur trioxide in nitrobenzene is uncertain, but probably it is monomeric. The approximate second order of the reaction with respect to sulphur trioxide implies that two molecules of the species predominantly present react, though whether as separate molecules or as a pair in the form of a molecule of S_2O_6 cannot yet be decided definitely. More evidence is required before the mechanism of the reaction can be further elucidated.

Bromination and Chlorination of Benzene, Toluene and Halogenobenzenes.

It is well known that while the halogenation of amines and phenols and their derivatives usually proceeds readily, halogenation of benzene itself and other substituted derivatives is slow unless a catalyst be employed, and may be complicated by the formation of addition products. The kinetics of such catalysed reactions have been the subject of a number of investigations. For example, Bruner²⁴ found that the bromination of benzene in excess hydrocarbon as solvent, with iodine as a catalyst, gives bimolecular constants, but these could not be related to the iodine concentration. His data has been recalculated by Price,²⁵ who showed that the reaction is better represented by the expression

$$dc/dt = k[\text{Br}_2]^{3/2}[\text{I}]^{1/2}.$$

He considers, therefore, that the mechanism of the reaction is represented by the scheme:²⁶



From the reaction kinetics, it is concluded that the catalyst molecule A is BrI_3 .

With toluene, studies of bromination have largely centred on the relation between nuclear and side chain substitution. Utilising the data of van der Laan,²⁷ Scheffer and Brandsma²⁸ showed that over the temperature range $25^\circ\text{--}75^\circ$ the change in proportions of *ortho* and *para* isomerides formed could be well reproduced by Equation (1), assuming, as in nitration, that the entropy term is zero. In an attempt to take into account the benzyl bromide formed simultaneously, the expression $\log k_o/k_k = 15,900/RT - 25.176$ was employed, where k_o and k_k refer to the formation of *o*-bromotoluene and benzyl bromide respectively. An approximate agreement with the change in yield of benzyl bromide over

²⁴ *Z. physikal. Chem.*, 1902, 41, 514.

²⁵ *J. Amer. Chem. Soc.*, 1936, 58, 2101.

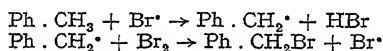
²⁶ Pfeiffer and Wizinger, *Ann.*, 1928, 461, 132.

²⁷ *Rec. trav. chim.*, 1905, 24, 1.

²⁸ *Ibid.*, 1926, 45, 522.

the range 25°-100°, as recorded by van der Laan, was obtained. However, Holleman and Pollak²⁹ have shown that the percentage of the total bromo-products consisting of benzyl bromide depends on the relative concentrations of the reactants. Thus with 4.3 molecules of toluene to 1 of bromine, 24 % of the total bromo-compounds consists of benzyl bromide, while with 28.5 molecules of toluene per molecule of bromine this figure is increased to 95 %. It is clear that the ratio of nuclear to side chain substituted products will vary continually as the bromine concentration changes during reaction, and the final proportion of benzyl bromide cannot be taken as a measure of the relative rate of side chain substitution. Consequently, the application of Scheffer's relation is, in this case, invalid.

Reviewing and extending older work, Kharasch, White and Mayo³⁰ conclude that so far as nuclear substitution is concerned the data are not inconsistent with the hypothesis of a bimolecular reaction between bromine and toluene, and exclude a mechanism involving bromine atoms. For the side chain reaction, partly on account of the discovery of a catalytic effect of peroxides, and the long known effect of light, a chain mechanism involving bromine atoms is proposed, such as :—



The halogenation of chloro- and bromobenzenes was studied by Holleman and van der Linden,³¹ who found that the relative rates of substitution in the *ortho*, *meta* and *para* positions appeared to depend on whether iron or aluminium is used as a catalyst, but traced the irregularity to interaction between the aluminium halides and the products of halogenation. More recently, studies have been made of the chlorination and bromination of halogenobenzenes at elevated temperatures, the reaction occurring in the gas phase or at a surface. Though strictly speaking the reaction is beyond the scope of the present discussion of reactions in solution, the results warrant some mention. Both in the absence of a catalyst and with pumice as catalyst, a remarkable change with temperature is found in the relative rates of substitution at the *meta* and *para* positions, as measured by the amounts of products formed.³² Below 400°,

TABLE II.

Temp.	% <i>Ortho</i> .	% <i>Meta</i> .	% <i>Para</i> .
400°	20	23	57
450°	20.5	54.5	25

bromination of bromobenzene yields the *para* compound as the chief product, while at about 450°, the proportion of *meta* compound is more than doubled, as shown by Table II. (pumice catalyst); in effect, a change from *ortho-para* to *meta* type of substitution has taken place, indicating a complete change of mechanism of substitution.

Indications of a similar effect for the chlorination of chlorobenzene³³ and for the bromination of fluoro- and chlorobenzene³² were also obtained. Analogous abnormal bromination of pyridine has also been

²⁹ *Rec. trav. chim.*, 1908, **27**, 435.³⁰ *J. Org. Chem.*, 1938, 333.³¹ *Rec. trav. chim.*, 1911, **30**, 305.³² Wibaut, van de Lande and Wallagh, *ibid.*, 1933, **52**, 794; Wibaut and van Loon, *ibid.*, 1937, **56**, 815.³³ Wibaut, van de Lande and Wallagh, *ibid.*, 1937, **56**, 65.

observed.³⁴ If the figures quoted actually represent the relative rates of substitution, and not merely the relative amounts of products surviving decomposition or further substitution, they represent a new phenomenon in benzene substitution reactions.

In contrast, the much more rapid bromination of bromobenzene over graphite impregnated with ferric bromide, or over iron gauze, proceeds normally. It is shown that over the extended temperature range of 200°-450° the variations in the proportions are accurately represented by Schaeffer's expression, with the entropy term, as before, equated to zero.³²

The Mechanism of the Bromination and Chlorination of Phenols and their Derivatives.

There exists much evidence that the ready bromination and chlorination of phenols is not always a direct reaction with the halogen molecule. As active intermediaries, the hypohalous acids, halogen atoms with or without a positive charge, and the trihalide ions have been suggested.

In general, phenols are most readily halogenated in polar solvents. For instance, Baines³⁵ finds that the bromination of phenol in carbon tetrachloride proceeds very slowly in the absence of water, but addition of water leads to the very rapid formation of tribromophenol. He therefore concludes that while the bromine molecule is but a weak brominating agent, the hypobromous acid formed by hydrolysis is very potent. On the other hand, Francis³⁶ finds that *m*-nitrophenol is brominated by bromine-water about 1000 times as fast as by aqueous hypobromous acid, and ascribes the activity of bromine-water to bromine atoms, probably carrying positive charges.

Schilov and Naniaev³⁷ also consider that the positive bromine ion is a very powerful brominating agent. This conclusion is based on measurements of the rate of bromination of anisole *m*-sulphonic acid (A) by hypobromous acid. In slightly alkaline solution, the reaction proceeds in accordance with the equation $d[\text{HOBr}]/dt = k_2[\text{A}][\text{HOBr}]$. As the acidity is increased by the addition of sulphuric or nitric acids, k_2 increases in value, but $k_2/[\text{H}^+]$ is approximately constant. Since the rate of reaction can be written $d[\text{HOBr}]/dt = k_1[\text{A}][\text{HOBr}][\text{H}^+]$, where $k_1 = k_2/[\text{H}^+]$, it is suggested that $[\text{HOBr}][\text{H}^+]$ is a measure of the formation of the bromine cation: $\text{HOBr} + \text{H}^+ \rightleftharpoons \text{Br}^+ + \text{H}_2\text{O}$. The possible effect of the hydrogen-ion concentration on the reactivity of the anisole *m*-sulphonic acid is not considered. Though no details are given, the following figures are stated to represent the velocity constants for the bromination by various agents of anisole *m*-sulphonic acid under the same conditions: HOBr, 0.12; Br₂, 80; BrCl, 43,000; Br⁺, 110,000.

The chlorination of phenols by hypochlorous acid has been studied by Soper and Smith³⁸ in aqueous solutions in which the hydroxyl-ion concentration is about 10⁻⁷, and in more strongly alkaline solutions (hydroxyl-ion concentration about 10⁻²). In the former case the speed of chlorination increases in direct proportion to the hydroxyl-ion concentration, and in the latter the speed is inversely proportional to the

³⁴ den Hertog and Wibaut, *Rec. trav. chim.*, 1933, 51, 381, 940; Burstall, *J.C.S.*, 1938, 1662.

³⁵ *J. Amer. Chem. Soc.*, 1925, 47, 2340.

³⁶ *Ibid.*, 1922, 2810.

³⁷ *Compt. rend. Acad. Sci. U.R.S.S.*, 1939, 24, 890.

³⁸ *J.C.S.*, 1926, 1582.

hydroxyl-ion concentration. It is therefore concluded that the reaction is either between the hypochlorite ion and unionised phenol, or between the unionised hypochlorous acid and the phenoxide ion. Detailed analysis of the kinetics of the reactions supports the second of these alternatives. If a little hydrochloric acid be added to a solution of phenol or a phenolic ether and hypochlorous acid, a rapid reaction ensues, the rate being independent of the phenol concentration, the chlorine generated reacting instantaneously with the phenol or phenol ether. Hypochlorous acid is without action on a phenol ether. The chlorine molecule is therefore a more powerful chlorinating agent than the hypochlorous acid molecule.

The subject has been re-examined by Alexander,³⁹ who overcame the difficulties presented by the extreme rapidity of halogenation in aqueous media by employing the ingenious monolayer technique.⁴⁰ *Para*-hexadecylphenol was used as a film-forming compound, and was spread on the appropriate aqueous substrate. The rate of reaction was calculated from the rate of change of surface pressure and surface potential. When the phenol was spread on dilute bromine water, the area-time curve was found to be unimolecular in shape, and the pseudo-unimolecular constant could be calculated. Addition of potassium bromide to the bromine-water substrate brought about a pronounced increase in reaction velocity, an increase which must be ascribed to the formation of tribromide ions. From the rates of reaction with bromine water plus varying amounts of bromide ion, and with hypobromous acid, the separate velocity coefficients for bromination by Br'_3 and HOBr may be calculated (assuming no other brominating agent is present, e.g., bromine atoms). It then appears that the tribromide ion is four times as effective as the hypobromous acid molecule.

From analogous experiments using chlorine water, with and without potassium chloride, and hypochlorous acid solution as substrates, it was calculated that the trichloride ion is about 10^3 times more active in chlorination than the hypochlorous acid molecule.

The experiments discussed above relate to aqueous solutions. In 50 % aqueous-acetic acid solution, on the other hand, it was found by Bradfield, Jones and Orton,⁴¹ who refer to earlier observation of the apparent inactivity of HBr_3 in bromination and oxidation reactions of bromine, that the bromination of phenolic ethers undergoes a marked retardation as hydrobromic acid is formed, or when it is added initially. Assuming that only the "free" bromine is active in bromination, the appropriate kinetic expression applied to the bromination of phenol ethers in experiments in which five or ten molecular proportions of hydrobromic acid were present at the start, gave bimolecular constants showing a slight downward drift as the reaction progressed. With smaller amounts of hydrobromic acid originally present, the drift in the constants becomes more marked. Addition of sodium bromide has almost exactly the same effect as hydrobromic acid, while addition of β -naphthalene sulphonic acid produced no change in the rate of reaction. Aqueous hypobromous acid mixed with acetic acid to bring the strength to 50 % or 75 % acetic acid brominates these ethers with extreme rapidity. The rate can only be followed with those ethers which are attacked by free bromine with extreme slowness in these media. The few experiments

³⁹ *J.C.S.*, 1938, 729.

⁴⁰ Alexander and Rideal, *Proc. Roy. Soc. A*, 1937, 163, 70.

⁴¹ *J.C.S.*, 1929, 2810.

made indicated that the reaction with hypobromous acid is bimolecular, though the reaction is too rapid for accurate measurement.⁴²

In contrast to the halogenation of phenols in water, and to the bromination of phenolic ethers in aqueous acetic acid, the reaction between phenolic ethers and chlorine in 99 % acetic acid appears to be a straightforward reaction, the chlorine molecule acting as the chlorinating agent. Employing the accurate method of chlorination of Orton and King,⁴³ it has been found that very satisfactory velocity coefficients may be calculated by the usual formulæ for bimolecular reactions, variations throughout an experiment being irregular and within the estimated experimental error of about 2 %.^{12, 44} As the proportions of chlorine to ether are changed from 1 : 1 to 1 : 10, the mean values of the velocity coefficients show a slight drift of about 5-10 %. The amount of hydrochloric acid present has little effect. Thus with *p*-chloroanisole, increase from 1.2 to 8 molecular proportions in the amount of hydrochloric acid added initially to liberate chlorine from the chloroamine used as a source of chlorine increases the velocity coefficient from 1.22 to 1.41. It does not appear, therefore, that in this medium the trichloride ion plays any significant part in the reaction, or indeed that any mechanism other than direct interaction between chlorine and ether comes into play. The rate, however, is very sensitive to the amount of water in the medium, the speed of chlorination of *p*-chloroanisole being increased by about 66 % as the amount of water in the medium is increased from 1 to 2 %.

The Chlorination of Phenolic Ethers.

It is well known that the speed of chlorination of both amines and phenols is considerably reduced by acylation. Alkylation of phenols reduces the speed to a smaller extent, while the introduction of halogen or a nitro-group still further deactivates anilides, phenol esters and ethers.

An extended series of measurements of the velocities of chlorination of phenolic ethers in 99 % acetic acid has been made by the method of Orton and King.⁴³ Although series of ethers of various types have been examined, the study has been limited mainly to the determination of the rates of chlorination of ethers in which either the *para* or the *para* and one *ortho* position are already occupied by such a group as CH₃, Cl, NO₂, etc. Not only is the speed of substitution so brought within the range of convenient measurement, but also, since only one product is obtained, the necessity of obtaining complementary information relating to the proportions of the isomerides formed is avoided.

Analysis of the results for ethers of the type *p*-RO . C₆H₄ . X, where both R and X were varied independently, showed (1) that the relative effects of a series of groups R₁, R₂, etc., are independent of the group X, and therefore necessarily (2) that the relative effects of a series of groups X₁, X₂, etc., are independent of the group R.¹² It is important to determine whether the changes in rate are due to changes in energies of activation or to changes in the *P* factor of the equation $k = PZe^{-E/RT}$, or in both. This information is derivable from the effect of temperature on the rates of reaction. Unfortunately the range of temperature over

⁴² G. Davies, *Thesis*, Univ. of Wales, 1931.

⁴³ *J.C.S.*, 1911, 1185.

⁴⁴ Orton and Bradfield, *ibid.*, 1927, 986.

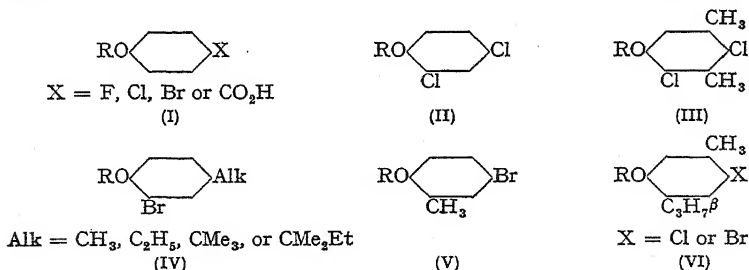
which the reaction can be accurately studied is limited on the one side by the freezing of the acetic acid medium, and on the other by the increasing loss of chlorine to the vapour phase as the temperature is raised. In practice, the range of 20°-35° was used. The result of such measurements by Bradfield, W. O. Jones and Spencer⁴⁵ is to show that the changes in rate brought about by variation in R and X are determined at least mainly by changes in E . The values of $\log k_1/k_2$ at one temperature were plotted against $\log k_1/k_2$ at the second temperature, and the slope and position of the line drawn through the points was compared with the slope and position of lines drawn to represent simple hypotheses by which the observed relative effects could be explained. Following Hinshelwood,⁴⁶ it is now customary to make the desired test by plotting $\log k$ against E , and comparing with a line of slope $-2.303RT$. The data of Bradfield, W. O. Jones and Spencer have been so plotted and included in a figure given by Hinshelwood, Laidler and Timms.⁴⁷ The points show (at least) a definite tendency to cluster along a line of this slope.

The method, particularly over so small a temperature range, is incapable of detecting small, though perhaps significant, simultaneous changes in P . However, the regular effects of substituents observed may be simply explained by assuming (1) that changes in rate due to changes in R, or to varying the substituents in the nucleus are due entirely to changes in the energy of activation, and (2) that the value of E is determined by the algebraic sum of characteristic quota contributed by R and X. For if

$$k_X^{\text{OR}_1} = PZe^{-(E_{\text{OR}_1} + E_X)/RT} \text{ and } k_X^{\text{OR}_2} = PZe^{-(E_{\text{OR}_2} + E_X)/RT},$$

then $k_X^{\text{OR}_1}/k_X^{\text{OR}_2} = e^{(E_{\text{OR}_2} - E_{\text{OR}_1})/RT}$, which is independent of X, and similarly, $k_{X_1}^{\text{OR}}/k_{X_2}^{\text{OR}} = e^{(E_{X_2} - E_{X_1})/RT}$, which is independent of R.* The velocities of chlorination of a considerable number of ethers have now been determined in order to examine the range of validity of this rule of additivity of E terms, and a general survey of the results will now be given.^{12, 45, 48}

It is found that the relative effects of substituents in the benzyl group of benzyl ethers are the same for ethers of all the types (I)-(VI) :—



⁴⁵ J.C.S., 1931, 2907.

⁴⁶ *Ibid.*, 1934, 1079.

⁴⁷ *Ibid.*, 1938, 850.

* $k_X^{\text{OR}_1}$ indicates the velocity coefficient for the chlorination of $\text{R}_1\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{X}$; E_{OR_1} indicates the contribution of the group OR_1 to the energy of activation, and so forth.

⁴⁸ Bradfield and B. Jones, J.C.S., 1928, 3073; 1931, 2903; B. Jones, *ibid.*, 1934, 210; 1935, 1831, 1835; 1936, 1854; 1938, 1414; 1941, 267, 358.

Values of the relative velocities for each series are shown in Table III, expressed in terms of the rate for the benzyl ether reckoned as 100.

TABLE III.—RELATIVE VELOCITIES FOR ETHERS OF A. C₆H₄.CH₂—

Ether Series.	A = H.	Para				Meta			o-Cl.
		CH ₃ .	Cl.	Br.	NO ₂ .	F.	Cl.	NO ₂ .	
I . . .	100	139	60	58	21	49	47	24	41
II . . .	100	—	—	—	—	—	45	—	—
III . . .	100	—	61	58	—	48	46	—	40
IV . . .	100	137	58	56	21	49	—	24	40
V . . .	100	139	61	59	21	48	45	—	41
VI . . .	100	136	62	61	—	—	—	—	—

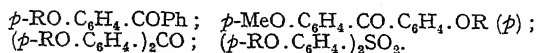
TABLE IV.

Ether Series.	<i>k</i> ^{20°} .	<i>E</i> (Cal.).	Ether Series.	<i>k</i> ^{20°} .	<i>E</i> (Cal.).
I (X = Cl) . .	0.419*	11,200	IV (Alk = Me)	3.92	9,700
II . . .	0.00223	(14,200)	V	2.28	(10,200)
III . . .	8.05	(9,500)	VI	174	(7,700)

* The value given is for *k*_{obs}/2, since there are two similar positions available for substitution in this series.

Taking *P* as constant, the difference in rates, within a series between the fastest (*p*-methylbenzyl ether) and the slowest (*m*-nitrobenzyl ether) corresponds to a variation in *E* of about 1100 Cal. Table IV shows the actual value of *k*_{obs} for the benzyl ether of each series and also the *E* values. The values in brackets are calculated from the relative velocities compared with *p*-chlorophenyl benzyl ether (Series I), for which the *E* value is known from experiment. The value for 3-bromo-*p*-tolyl benzyl ether (Series IV) is also an experimental value. It is seen from Tables III and IV that although the actual rates and the magnitudes of the energies of activation vary over a wide range when one series is compared with another, the relative rates, and therefore the energy differences, are remarkably constant.

In Table V are shown the relative rates for alkyl ethers, now for convenience taking the value for the methyl ether as 100. The value for the benzyl ether is included to link Tables III and V. In this group values are also available for compounds of the types:—



Effects of R for each of these types are almost identical, and the mean values are recorded in Table V as Series VII.

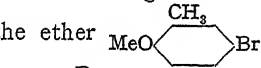
It is seen that here some departure from the rule of strict constancy of velocity ratios obtains. This departure, of the order of 10-20 %, seems to be connected with the presence of one or more alkyl groups in the nucleus undergoing chlorination (Series III, IV, and V). The irregularities are too small for it to be possible to determine whether they arise from variation in the *P* factor or from lack of strict additivity

of the *E* terms. Taken as a whole, however, the figures in Tables III and V show a degree of uniformity in the effect of groups on reactivity which was quite unforeseen when the work was begun some fifteen years ago.

TABLE V.

Ether Series.	R = Me.	Et.	Pr ^α .	Pr ^β .	C ₆ H ₅ · CH ₂ .
I (X = Cl, Br, NO ₂ or CO ₂ H)	100	199	223	440	68
II	100	199	217	—	69
III	100	185	195	—	57
IV	100	185	—	—	55
V	100	197	210	325	54
VII	100	201	221	488	—

As already pointed out, the regularity of the effects of X (the one or more nuclear substituents present) follows automatically from the observed regularities in the effect of R, and to the same degree of accuracy. It should be noted, however, that the ether

chlorinates at 0.612 of the rate of the isomeric ether . Evidently due regard must be paid to nuclear position in compounding effects of groups.

Attempts have been made to carry out a parallel series of measurements with anilides.^{44, 48, 49} However, the reaction between anilides and chlorine in the presence of hydrochloric acid is not kinetically strictly of the second order, the calculated velocity coefficients varying in a somewhat irregular manner with change in the initial molecular proportions of the reactants and in the concentration of the hydrochloric acid. These irregularities are perhaps due to interaction of the anilido-group with the acid environment. Indications of approximate additive effects can be observed, however.

The Relation Between the Effects of Substituents in Benzene Substitution and Other Reactions.

It is of interest to make some comparisons of the data for the chlorination of ethers with that obtained in the study of other reactions. In recent years a striking regularity in the effects of substituents in a benzene ring on the rates of a number of reactions in which a group attached to the ring participates has been illustrated by plotting values of $\log k$ for the reaction in question against $\log K$, K being the dissociation constant for the correspondingly substituted benzoic acid. In a number of cases a linear relationship obtains, *i.e.*, $\log k = \alpha \log K + \text{constant}$.^{50, 51} An alternative procedure is to plot $\log k$ for one reaction against $\log k$ for a second. In Fig. 1, curves I, II, III, and IV, the values of $\log k$

⁴⁹ B. Jones, *J.C.S.*, 1936, 1231.

⁵⁰ Hammett and Pfluger, *J. Amer. Chem. Soc.*, 1933, 55, 4079; Hammett, *ibid.*, 1937, 59, 96; *Chem. Reviews*, 1935, 17, 125; *Trans. Faraday Soc.*, 1938, 34, 156.

⁵¹ Burkhardt, Ford and Singleton, *J.C.S.*, 1936, 17.

for the velocity coefficients for the chlorination of a series of *p*-alkoxybenzophenones substituted in the *m*'- and *p*'-positions are plotted against $\log k$ for several typical reactions affecting a group attached to a benzene nucleus. It will be seen that in all cases the points approximate closely to a straight line. The values of $\log k$ for the alkaline hydrolysis of substituted benzamides, employed in the construction of curve II, are among those which have been shown to exhibit a linear logarithmic relationship to the dissociation constants of the substituted benzoic acids.⁵¹ It follows, therefore, as a matter of course that as curve II is a straight line, a linear relationship exists between $\log k$ for the substituted alkoxybenzophenones and $\log K$ for substituted benzoic acids, and between $\log k$ for these ethers, and any other set of values of $\log k$ showing a linear relationship to $\log K$.

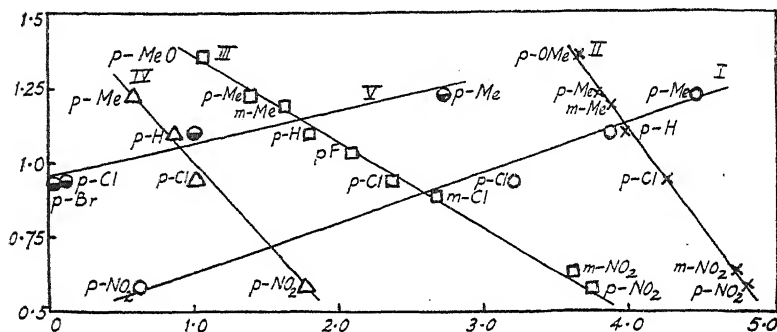


FIG. 1.

Ordinate.—($\log k^{250} \times 10$) for the chlorination of substituted benzophenones.

Abscissa.—

I.— $\log (k^{250} \times 10^5)$ for the benzylation of substituted anilines.⁵² Points O.

II.— $\log (k^{1000} \times 10^5)$ for the alkaline hydrolysis of substituted benzamides.⁵⁴ Points X.

III.— $\log (k^{250} \times 10^5)$ for the alkaline hydrolysis of esters of substituted benzoic acids.⁵³ Points □.

IV.— $\log (k^{250} \times 10^3)$ for the benzylation of aniline with substituted benzoyl chlorides.⁵² Points Δ.

V.— $\log (F^{180} \times 10)$ for the nitration of benzene, toluene, chloro- and bromobenzene.¹⁸ Points ●.

The figures shown in Table VI for the relative effects of substituents in ring II of alkoxybenzophenones and in the benzyl nucleus of benzyl ethers are sufficient in themselves to show that the effects of substituents are very similar in the two series of ethers, and a plot of $\log k$ for the benzyl ethers has not, therefore, been included in the figure. In the benzyl series of ethers the effect of *m*-CH₃ is slightly greater, and in the alkoxybenzophenones slightly less than the effect of *p*-CH₃, but the differences are too small to disturb appreciably the linearity of the logarithmic relationships.

It is of particular interest that the effects of substituents in the benzyl group of benzyl ethers or in ring II of the alkoxybenzophenones are thus closely related to the effects of the same substituents in such

⁵² Williams and Hinshelwood, *J.C.S.*, 1934, 1079.

⁵³ Ingold and Nathan, *ibid.*, 1936, 222; Evans, Gordon and Watson, *ibid.*, 1937, 1430.

⁵⁴ Reid, *Amer. Chem. J.*, 1900, 24, 203.

reactions as the benzylation of amines and the hydrolyses of benzoic esters and amides, for in the ethers the substituent in question is not connected to the seat of reaction by a conjugated system. The contrast in the paths available for transmission of effects is still more marked when the effects of CH_3 , H , Cl and Br on the rates of chlorination of these ethers are compared with the partial rate factors for the nitration in the p -position of toluene, benzene, chloro- and bromobenzene (curve V), but even here, so far as can be judged from so few points, an approximately linear relationship exists. The damping effect of the interposed saturated atoms in the ethers is shown, however, by the fact that the value of F for the nitration of toluene in the p -position is 396 times the value of F for chloro-benzene, while the p -methylbenzyl ether of p -chlorophenol chlorinates at only 2.36 times the rate of the p -chloro-benzyl ether.

Considering now the effects of aliphatic radicles attached to the phenolic oxygen atom on the rates of chlorination, only a limited comparison with other data is possible. A few values for the relative rates of bromination of ethers are available, for although the specific mechanism of the reaction between bromine and phenolic ethers in aqueous acetic acid is not yet clear, Bradfield, Jones and Orton were able to measure the relative rates of bromination in 50 % acetic acid of several ethers by direct comparison of the times taken for a given percentage change, in experiments in which the initial concentrations of the reactants were identical.⁴¹ The relative rates found for the bromination of the methyl, ethyl and isopropyl ethers of p -chloro- and p -bromophenol in 50 % acetic acid are 100 : 229 : 712. It has been pointed out that these figures may be connected with the relative rates of chlorination of the same ethers in 99 % acetic acid by the expression $0.775 \log r_B = \log r_C$, where r_B and r_C are the relative rates of bromination and chlorination respectively.⁵⁵ In 75 % acetic acid the relative rates of bromination of the benzyl, methyl, ethyl, n -propyl, and iso -propyl ethers of p -chlorophenol are

$$55 : 100 : 255 : 336 : 840.^{42}$$

These figures may similarly be connected with the relative rates of chlorination by means of the expression $0.695 \log r_B = \log r_C$. These expressions are, of course, another form of the linear logarithmic relationship.

Again, it has been shown that the relative effects of three alkoxy- and one benzyloxy groups as given by the proportions of isomerides formed in the nitration of quinol ethers of the type $p\text{-RO} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ ⁵⁶ can be approximately related to the effects of the same groups on the speed of chlorination by an expression of the same form, viz. $\log r_1 = \alpha \log r_2$.⁵⁷

The physical significance of the linear logarithmic relationship has been discussed by Polanyi⁵⁸ and by Hinshelwood⁵⁹ from the standpoints of the transition state and kinetic methods of treating reaction velocity. Following the kinetic method, it is pointed out that for two series of reactions in each of which the PZ term is constant, the implication of

⁵⁵ Bradfield and B. Jones, *J.C.S.*, 1931, 2903; Bradfield, *Nature*, 1934, 134, 421.

⁵⁶ Robinson and Smith, *J.C.S.*, 1926, 392; Clarke, Robinson and Smith, *ibid.*, 1927, 2647.

⁵⁷ Bradfield and B. Jones, *ibid.*, 1928, 3073.

⁵⁸ *Ibid.*, 1937, 634.

⁵⁹ *Ibid.*, 639.

the linear logarithmic relation is that $\Delta E_1 = \alpha \Delta E_2$. The experimental results show that the value of α is altered from one reaction (or equilibrium) to another. That is, the effects of substituents on the energies of activation are not represented by quantities of fixed magnitude, but by quantities which are fractions of some maximum, the fractional coefficient α being determined, apparently, by (1) the path by which the effect reaches the point of reaction, (2) the nature of the other reactant, and (3) the environment during reaction.

For the chlorination of ethers under the given conditions, the values of the coefficients α and α' , representing the fractions of the maximum effects of substituents of the two series R_1, R_2 , etc., and X_1, X_2 , etc., on E , are constant. For then the observed energies of activation are $E_1 = (\epsilon_0 + \alpha\epsilon_{R_1} + \alpha'\epsilon_{X_1})$; $E_2 = (\epsilon_0 + \alpha\epsilon_{R_2} + \alpha'\epsilon_{X_1})$, etc., for a series of ethers the members of which all contain the substituent X_1 ; and $E'_1 = (\epsilon_0 + \alpha\epsilon_{R_1} + \alpha'\epsilon_{X_2})$; $E'_2 = (\epsilon_0 + \alpha\epsilon_{R_2} + \alpha'\epsilon_{X_2})$, etc., for a series in which X_2 replaces X_1 . E_1 and E_2 may differ considerably from E'_1 and E'_2 , but $\Delta E = \Delta E'$, as required.

It is not proposed to review qualitatively the mass of data collected relating to the effect of substituents on the rates of chlorination of ethers in the light of the electronic theory of reactions, since the results are in general harmony with the requirements of the theory. Opportunity is taken, however, to collect in synoptic form figures representing the relative effects of substituents on reactivity. The figures shown in Table VI represent the relative rates of chlorination at a single carbon atom. Where necessary, in comparisons, allowance is made for the unequal number of positions available for chlorination, *e.g.*, the relative effects of CH_3 and H obtained from a comparison of the rates of chlorination of

(1) $\text{RO}-\text{C}_6\text{H}_4-\text{Br}$, and (2) $\text{RO}-\text{C}_6\text{H}_3(\text{CH}_3)-\text{Br}$ are expressed by $2k_2/k_1$, where k_1 and k_2 are the observed velocity coefficients for (1) and (2) respectively. The numerical values given are subject to small variations in certain types of ethers, as mentioned earlier.

TABLE VI.—RELATIVE RATES OF CHLORINATION IN 99 % ACETIC ACID AT 20°.

I. Comparison of Groups Directing Chlorine to the *Ortho* Position.

- (a) Comparison of (i) $p\text{-MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{Cl}$ (ii) $p\text{-Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{NHCO} \cdot \text{C}_6\text{H}_5$.
(iii) $p\text{-Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{OOC} \cdot \text{C}_6\text{H}_5$.

Relative rates 100 : 25 : $\sim 10^{-3}$.

- (b) Effects of variation in the group *R* of ethers.

(i) Straight chain alkyl groups.

Alkyl group	$\cdot\text{CH}_3$	$\cdot\text{C}_2\text{H}_5$	$\cdot\text{C}_3\text{H}_7$	$\cdot\text{C}_4\text{H}_9$	$\cdot\text{C}_5\text{H}_{11}$	$\cdot\text{C}_6\text{H}_{13}$
Relative rates	100	199	222	222	221	221
Alkyl group	$\cdot\text{C}_7\text{H}_{15}$	$\cdot\text{C}_8\text{H}_{17}$	$\cdot\text{C}_9\text{H}_{19}$	$\cdot\text{C}_{10}\text{H}_{21}$	$\cdot\text{C}_{16}\text{H}_{33}$	
Relative rates	218	207	203*	203*	201	

(ii) Branched chains.

Alkyl group	$\cdot\text{C}_3\text{H}_7$	$\cdot\text{C}_4\text{H}_9(\text{iso})$	$\cdot(\text{CH}_2)_2\text{Br}$	$\cdot(\text{CH}_2)_3\text{Br}$
Relative rates	440	216	21	65

(iii) ω -Bromoalkyl groups.

(iv) ω -Phenyl groups.

Group	$\cdot\text{CH}_2\text{Ph}$	$\cdot(\text{CH}_2)_2\text{Ph}$	$\cdot(\text{CH}_2)_3\text{Ph}$
Relative rates	68	119	171

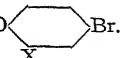
* Unpublished results (B.J.).

TABLE VI.—(continued).

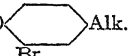
II. Relative Effects in Ethers of Other Substituents Directly Attached to the Nucleus undergoing Chlorination.

(a) Comparison of substances of the type : $p\text{-RO} \cdot \text{C}_6\text{H}_4 \cdot \text{X}$.

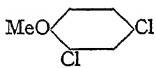
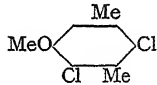
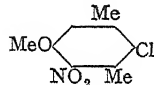
Group X	$\cdot\text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$	$\cdot\text{F}$	$\cdot\text{CO} \cdot \text{C}_6\text{H}_5$	$\cdot\text{Br}$	$\cdot\text{Cl}$
Relative rates	528	521	287	280	273
Group X	$\cdot\text{CO}_2\text{Et}$	$\cdot\text{CO}_2\text{Me}$	$\cdot\text{CO}_2\text{H}$	$\cdot\text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$	$\cdot\text{NO}_2$
Relative rates	189	165	100	12.4	0.68

(b) Comparison of substances of the type : 

Group X	$\cdot\text{CH}_3$	$\cdot\text{H}$	$\cdot\text{Br}$
Relative rates	694	100	0.62

(c) Comparison of substances of the type : 

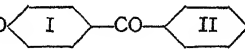
$p\text{-Alkyl group}$	$\cdot\text{CH}_3$	$\cdot\text{C}_2\text{H}_5$	$n\text{-C}_3\text{H}_7$	$\cdot\text{CMe}_3$	$\cdot\text{CMe}_2\text{Et}$
Relative rates	100	121	93	49	41

(d) Comparison of			
	(I)	(II)	(III)
Relative rates	0.0228	100	0.274

III. Relative Effects in Ethers of Substituents not Directly Attached to the Nucleus undergoing Chlorination.

(a) Substituent in the benzyl group of benzyl ethers, referred to the unsubstituted benzyl group as 100.

	$\cdot\text{CH}_3$	$\cdot\text{F}$	$\cdot\text{Cl}$	$\cdot\text{Br}$	$\cdot\text{NO}_2$
Ortho	148	51	41	—	21
Meta	151	48	46	48	24
Para	139	82	61	59	21

(b) Substituent in ring II of ethers of the type :  referred to the alkoxy-benzophenone as 100.

	$\text{CH}_3\text{O} \cdot$	$\cdot\text{CH}_3$	$\cdot\text{F}$	$\cdot\text{Cl}$	$\cdot\text{Br}$	$\cdot\text{NO}_2$
Ortho	—	—	47	37	37	—
Meta	—	122	62	—	62	34
Para	184	133	85	69	68	30

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GENERAL DISCUSSION

Dr. A. E. Bradfield (London) said, in introducing the paper: In the substitution reactions of benzene derivatives there is a consistency and regularity in the relation between reactivity and structure which is much more obvious than it is, for example, in aliphatic substitution and elimination reactions. There is every reason to believe that the familiar processes of nitration, sulphonation and halogenation proceed by simple bimolecular mechanisms, free from intrusions of unimolecular mechanisms. This conclusion is reached from a consideration of the observed regularities rather than from a detailed knowledge of the reaction kinetics, for experiment has shown that often these aromatic substitution reactions are by

no means simple kinetically, with the result that even the nature of the substituting entities is to some extent conjectural. In spite of this gap in our knowledge, it has been possible in this field to raise some of the observed regularities to the approximately quantitative level, and it is of interest to examine a few further examples of these regularities.

It has been shown that the effects of NO_2 , Hal., H and CH_3 attached to ring II of substituted alkoxybenzophenones, or to the benzyl group of benzyloxyphenols, may be correlated by means of the linear logarithmic relationship with the effects of the same substituents on the rates of such reactions as, for example, the hydrolysis of esters of substituted benzoic acids. When these same substituents are attached to the phenolic nucleus undergoing chlorination, they exert very much more powerful effects on the speed of the reaction. For instance, while *p*-nitroanisole chlorinates very slowly and *p*-chloroanisole at a moderate speed, anisole (with a *p*-hydrogen atom) and *p*-tolyl methyl ether chlorinate with such extreme rapidity that the reaction cannot be followed by ordinary methods. However, values for the relative effects of NO_2 , Cl, H and CH_3 attached to carbon 2 of phenolic ethers on the rate of chlorination at carbon 4, may be derived by combining the data for the relative effects of (1) H and Cl in 4-chloro- and 2:4-dichloroanisole, (2) Cl and NO_2 in 2-chloro-4-methyl and 2-nitro-4-methyl anisole, and (3) H and CH_3 in 4-bromoanisole and 2-methyl-4-bromoanisole, respectively. The values so obtained (denoted by r_2) are shown in the first line of Table IV. It should be noted that the combination of these ratios to give the complete sequence involves the assumption that the relative effects of groups attached to carbon 2 are independent of the group attached to carbon 4. This assumption is an extension of the rule of additivity of *E*-terms discussed in the paper. Comparison with the relative effects on the speed of chlorination of the same groups in the *m'*-position of alkoxybenzophenones (values denoted by r_{BP} , line 2) shows that in the former case the range of speeds is greater by no less than 10^5 than in the latter. The following relationship exists between the values of r_2 and r_{BP} :

$$\log r_{\text{BP}} = 0.0988 \log r_2. \quad (1)$$

The values of r_{BP} calculated by this expression are shown in the third line of Table V.

TABLE V

	NO_2 .	Cl.	H.	CH_3 .
r_2	1.00	2.40×10^2	4.60×10^4	3.20×10^5
r_{BP}	1.00	1.77	2.86	3.50
r_{BP} (calc.)	1.00	1.72	2.89	3.50

Similarly the values of r_2 may be connected with $r_{\text{Benz.}}$, representing the relative rates of chlorination of *m'*-substituted benzyl ethers by means of the expression:

$$\log r_{\text{Benz.}} = 0.128 \log r_2. \quad (2)$$

The agreement here (Table VI) is not quite so good as in the previous case, and with the CH_3 group, a definite divergence occurs.

TABLE VI

	NO_2 .	Cl.	H.	CH_3 .
$r_{\text{Benz.}}$	1.00	1.91	4.29	6.49
$r_{\text{Benz.}}$ (calc.)	1.00	2.02	3.95	5.06

The effects of these groups (as *m*-substituents) on the rates of hydrolysis of benzoic esters cover a range intermediate between the two extremes considered above. Table VII shows in line 1 the relative rates of ester hydrolysis, r_H , while line 2 shows the values of r_H calculated from the expression :

$$\log r_H = -0.3945 \log r_2 \quad . \quad . \quad . \quad (3)$$

It will be seen that again the experimental and calculated values for the methyl group are not in good agreement.

TABLE VII

	NO ₂ .	Cl.	H.	CH ₃ .
r_H	1.00	0.111	0.0145	0.0101
r_H (calc. from 3) . . .	1.00	0.115	0.0145	0.0068
r_H (calc. from 4) . . .	1.00	0.122	—	0.0091

From the existing data, values for the effects of substituents attached to carbon 4 of the phenolic nucleus can only be obtained for NO₂, Cl, and CH₃. From the figures obtained, *viz.*, 1.00, 4.10×10^2 , 6.75×10^5 , values of r_H calculated by the expression :

$$\log r_H = -0.350 \log r_4 \quad . \quad . \quad . \quad (4)$$

are shown in line 3 of Table VII.

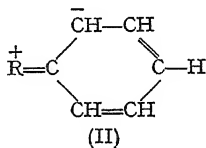
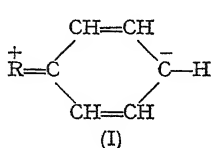
Both in the benzyl ethers and the alkoxybenzophenones, and also in the phenolic nucleus, the substituents are so placed that they are unable to initiate directly electromeric changes assisting the substitution reaction, and it would seem that it is the polarisation induced by the substituents which is the determining factor and which exhibits this regularity. It has been pointed out that the partial rate factors for the *para* nitration of toluene, benzene and the halogenobenzenes show an *approximately* linear relationship to the effects of CH₃, H and Hal. in the alkoxybenzophenones. This signifies, perhaps, that the major differences in speeds of nitration are primarily determined by polarisation effects. Polarizability, which is here possible, probably plays a more important part in determining the relative rates of *ortho* versus *meta* or *para* substitution.

Attention may be drawn to another point of interest in connection with the relative effects of alkyl groups attached to phenolic oxygen. As is to be expected, for chlorination, bromination and nitration, the rate measurements place the alkyl groups in a sequence corresponding to the operation of the general inductive effect. When attached to carbon 4 of the phenolic nucleus, the differences between the effects of the various alkyl groups on the speed of chlorination of ethers are smaller than when they are attached to oxygen, and, moreover, the sequence is now Me < Et > Pr^α > Bu^γ > Amyl^γ. The effect is still essentially a polarisation effect, but in contrast to the previous case, the mesomeric polarisation opposes the inductive effect differentially as between one group and another, so that not only is the ratio Et/Me reduced from 1.99 to 1.21, but also the ethyl group represents a maximum in the series. A precisely similar sequence is theoretically to be expected for the effects of alkyl groups attached in the *p*-position to the benzyl ring of benzyl ethers, but with the already diminished differences enormously reduced. It is not surprising, therefore, that Brynmor Jones found that in this case no differences are experimentally detectable.

Dr. W. A. Waters (*Durham*) said : The *meta* dibromination of benzene at high temperatures is probably a reaction of bromine atoms since (a) thermal dissociation of molecular bromine is possible under these

circumstances and (b) the polar substitution laws do not hold and one finds that the *meta/para* ratio is 2/1, which is the figure deduced from collision probabilities.¹ The low percentage of *ortho* substitution may be due, in part, to steric effects, but the production of rather a low percentage of the *ortho* isomer is a general feature of aromatic substitution, which is particularly evident in the polar substitution of compounds containing *ortho/para* directing groups. With these compounds the *ortho/para* ratio never rises to the statistical value of 2/1.

A symmetry factor conditioning energy levels in the mesomeric structures of aromatic compounds may be operative here. Thus a symmetrical form (I) may well have a lower energy content than an unsymmetrical form (II) in which the bulk of the aromatic ring lies to one side of the developed polar charges. Should this be so then the probability of the activated state being symmetrical, and largely (I) would be greater than for it being largely (II).



Dr. Bradfield, in reply, said: I agree with Waters's remarks. Hypotheses concerning the magnitude of the *ortho/para* ratio can, of course, be "inverted" for the consideration of *meta* substituting compounds, since these contain substituents which deactivate the *para* position more than the *ortho* position.

Prof. C. K. Ingold said: I wish to support Waters's and Bradfield's arguments with respect to the importance of the symmetry factor on the *ortho/para* ratio, though I think this factor affects the transition probability more than the energy of Waters's quinonoid structures (I) and (II), i.e., of excited states approximating to these structures. The probability is as important as the energy in determining the capacity of the system for the perturbations needed to form the transition states of substitutions.²

Dr. Gwyn Williams (London-Bristol) (communicated): Benford and Ingold³ have pointed out that the agent in nitration is probably a molecule of the type $\text{X}-\text{NO}_2$, where X is an electron attracting group and the NO_2 group is positively polarised. As a logical extension, the nitronium cation should be a potent nitrating agent,⁴ if the conditions of reaction allow it to exist. In connection with Bradfield and Jones's comments upon the nature of the nitrating agent in aromatic nitration, it is therefore interesting to note that Russian authors⁵ have recently supported the view that the nitrating agent is a nitronium cation.

Hantzsch⁶ emphasised that the strong mineral acids differ in acid strength and determined the order $\text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{HNO}_3$; and Kolthoff and Willman⁷ deduced the same order from conductivity

¹ Cf. Waters, *This vol.*, p. 772.

² Cf. Hughes and Ingold, *J. Chem. Soc.*, 1941, 612.

³ *J. Chem. Soc.*, 1938, 929.

⁴ Cf. Brewin and Turner, *ibid.*, 1928, 334; P. V. Youle, Ph.D. Thesis, Sheffield, 1937.

⁵ Ussanowitsch, *J. Gen. Chem. Russia*, 1940, 10, 219; Ussanowitsch and Abidov, *ibid.*, 223; Ussanowitsch and Glouchov, *ibid.*, 227; Ussanowitsch and Sushkevitsch, *ibid.*, 230; Ussanowitsch, *Acta Physicochim. U.R.S.S.*, 1935, 2, 239.

⁶ Hantzsch and Weissberger, *Z. physikal. Chem.*, 1927, 125, 251; Hantzsch and Voigt, *Ber.*, 1929, 62, 975; Hantzsch and Langbein, *Z. anorg. chem.*, 1932, 204, 193; Hantzsch, *ibid.*, 1932, 205, 163.

⁷ Kolthoff and Willman, *J. Amer. Chem. Soc.*, 1934, 56, 1007. Cf. Hall, *Chem. Reviews*, 1931, 8, 191.

measurements in acetic acid, in which nitric acid behaves as a weak electrolyte. Hantzsch⁸ also established the existence of nitronium cations by isolating crystalline nitronium perchlorates $[\text{NO}(\text{OH})_2]^+\text{ClO}_4^-$ and $[\text{N}(\text{OH})_2]^{++}(\text{ClO}_4)_2^{--}$ and by showing⁹ that, on electrolysis of nitronium perchlorate in nitromethane solution, nitric acid accumulated at the cathode. Nitronium bisulphate was shown to exist in nitric-sulphuric acid mixtures.⁸ The nitronium perchlorates correspond to the crystalline hydroxonium perchlorate $[\text{OH}_2]^+\text{ClO}_4^-$.¹⁰

Applying these considerations to nitrating acids, Ussanowitsch and co-workers⁵ point out that aromatic nitration is facilitated by mixing nitric acid with substances (*e.g.*, H_2SO_4) towards which it acts as a base and hindered by mixture with substances (*e.g.* water, nitrobenzene) towards which it acts as an acid. They conclude that nitrate ions do not nitrate aromatic compounds and that the nitrating agent is the nitronium cation. On the other hand, the nitration of aliphatic compounds¹¹ is assisted by addition of water or acetic acid and here they consider the nitrating agent to be the nitrate ion.

Experimentally, the authors have examined the nitration of toluene at 90°, in nucleus and side-chain, by nitric acid mixed with varying proportions of each of a number of solvents. Increasing proportion of monochloroacetic acid and ethyl nitrate, towards which nitric acid displays no acid or basic function, lowers the yields of both side-chain and nuclear nitrated products obtained in a given time; but increasing proportion of acetic acid and nitrobenzene lowers the yield of nitrotoluenes and increases that of phenylnitromethane; whilst sulphuric and trichloroacetic acids direct nitration almost exclusively into the nucleus. Nitric acid evidently acts as an acid towards acetic acid and nitrobenzene, and as a base towards sulphuric acid; but the conclusion that it acts as a base towards trichloroacetic acid may be in conflict with the results of Hantzsch,⁸ according to which trichloroacetic acid is a weaker acid than nitric acid.

Dr. H. O. Jenkins (*communicated*): The influence of substituents on the alkaline hydrolyses of a series of *p*-substituted ethyl benzoates has been examined previously by plotting the energy of activation *E* against the calculated electrostatic potential ψ due to the substituent dipole, at the carbon atom to which the ester grouping is attached.¹² The changes in energies of activation have been referred to differences in the amounts of work required to bring up hydroxyl ions against dipole fields, and the usual mechanism of alkaline ester hydrolysis given some quantitative support.

In a private communication Bradfield has invited me to apply this method to the study of the effect of substituents attached to the phenolic nucleus undergoing chlorination in the *m*-position to the substituent. The data therefore of Bradfield and Jones for the relative effects of the NO_2 , Cl, H, and CH_3 groups attached to carbon 2 of the anisole nucleus on the rate of chlorination at carbon atom 6 has been taken, and plotted against the electrostatic potential at carbon 6 due to each substituent dipole at carbon 2. As the above-mentioned authors have explained, the data of the complete sequence are partly derived using the well-established law of additivity of *E* terms. It is $\log r_2$ (see Bradfield's Introduction) which is plotted against ψ , the justification for this being the approximate constancy of the *PZ* term of the Arrhenius expression. The flat curve I is obtained, but the departure from linearity is not great (although it may well be a real effect (see Fig.) considering the range of r_2

⁸ Hantzsch, *Ber.*, 1925, 58, 941.

⁹ Hantzsch and Berger, *ibid.*, 1928, 61, 1328.

¹⁰ Volmer, *Annalen*, 1924, 440, 200.

¹¹ Konowalow, *Ber.*, 1895, 28, 1852; Markownikoff, *ibid.*, 1899, 32, 1441; 1900, 33, 1905.

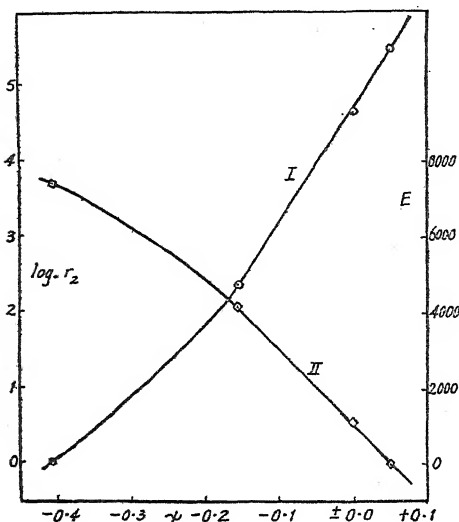
¹² Jenkins, *J.C.S.*, 1939, 1780.

which is 10^5 . Similar graphs could be drawn for the effects of substituents attached to carbon atom 4 of the phenolic nucleus, and to represent the relative rates of chlorination of substituted alkoxybenzophenones and benzyl ethers. Again using equations of the form

$$\ln k_{Me} - \ln k_{NO_2} = \frac{E_{NO_2} - E_{Me}}{RT}$$

relative energies of activation have been calculated for the anisole series with the substituents at carbon 2. These are given in the Table and plotted in Curve II.

As is to be expected a flat curve is also obtained. The main point of interest, however, lies in the difference of 7360 cal. when the substituent is changed from NO_2 to CH_3 , which provides a guide as to the mechanism of the reaction. Since the substituents are not in a position to directly initiate electromeric changes affecting the reaction, Bradfield drew the conclusion that it is the polarisation induced by them which is the determining factor affecting the relative rate, and this is supported by the present method of treating the results.



The usual statement, however, as to the mechanism of the chlorination of phenolic ethers in 99 % acetic acid surely needs some modification. In the hydrolyses of *p*-substituted ethyl benzoates $E_{Me} - E_{NO_2}$ was found experimentally to be 3700 cal. The corresponding difference 7360 cal. in the chlorination example is of the same order of magnitude, and the inference is that the attacking body is again an ion and not a partially polarised chlorine molecule, *i.e.* a dipole,

Substituent.	E (cal.)	ψ .
NO_2 . . .	7360	- 0.408
Cl . . .	4180	- 0.158
H . . .	1130	\pm 0.000
CH_3 . . .	0	+ 0.050

which would provide an insignificant work term. The ion would also have to be positive in sign. It is realised that the chlorination reactions are more complex than the hydrolyses, but there is a similarity in the effects of substituents which implies some similarity in mechanism.

Dr. Brynmor Jones (*Sheffield*), in reply, said: In the earlier stages of the kinetic study of the chlorination of phenolic ethers it was expected that the observed regularity in the relative effects of groups attached to the oxygen atom and of substituents in the nucleus would only be maintained within a narrow range of ethers. Subsequent extension of the work to include a wide variety of ethers has so far, however, brought to light only minor anomalies.

The regularities have been explained by assuming that for all the compounds examined the term P of the expression $k = PZe^{-E/RT}$ remains constant, and further, that each group contributes a characteristic quota to the critical energy increment. That the influence of groups is, in fact,

mainly on *E* was shown by Bradfield, Jones and Spencer in 1931 when a study of the velocities of chlorination at 20° and 35° was made.

Latterly attention has been turned to a re-examination of the question of the constancy of the term *P* with a view to determining the precision with which the earlier conclusion may be applied to the much wider range of ethers since investigated.

At present results are available only for ethers of the simple type *p*-RO . C₆H₄ . X, where R is an alkyl or benzyl group and X is F, Cl, NO₂ or CPh. For the ten ethers of this type selected for detailed study, the energies of activation, calculated from the rates of chlorination measured at five temperatures between 15° and 35°, vary from 9,600 to 14,300 cal. On plotting log₁₀ *k* against *E*, it is found that the series of approximately equally spaced points all fall on or very near to a line of slope $-2.303RT$. Up to the present the only disubstituted ether examined is 2 : 4-dichloroanisole, and this, too, gives a point on the line.

These new measurements (a fuller account of which will be published elsewhere) fully confirm the original conclusion, *viz.*, that the influence of substituents is to be ascribed almost entirely to changes in the energy of activation.

It is proposed later to extend this investigation to di- and poly-substituted phenolic ethers.

MECHANISM AND KINETICS OF ADDITIONS TO OLEFINIC COMPOUNDS.

BY GWYN WILLIAMS.

Received 3rd September, 1941.

The common assertion, that the olefinic double bond is a "point of weakness" in the molecule, is acceptable as a shorthand statement that the formation of addition compounds is the characteristic property of "unsaturated" substances; but it may be misleading if taken to imply that addition reactions are specially easy or straightforward. Thus, although addition of halogens at the double bond is one of the most general reactions of olefinic compounds, yet equal emphasis should be placed on the extreme variation of reactivity displayed by different olefin derivatives towards halogens.¹ And the quantitative celerity of halogen addition to certain olefins (*e.g.* ethylene, styrene) is itself deceptive if taken to signify that the reaction mechanism is simple. On the contrary, considerable complexity is revealed by kinetic investigations, whose sum total goes to show that, far from being an automatic trap for unwary halogen, the double bond is rather an objective to be sprung only by subtle and devious attack.

Electronic Interpretation of Halogen Addition.

It seems to be well established that halogen addition represents attack by positively polarised (cationoid or electrophilic) halogen upon a negative centre at one of the unsaturated carbon atoms.² Experimental evidence for this statement is as follows:—

¹ Sudborough and Thomas, *J. Chem. Soc.*, 1910, 97, 715, 2450; D. M. Williams and James, *ibid.*, 1928, 343.

² Burton and Ingold, *ibid.*, 1928, 904; Robinson, *J. Soc. Dyers and Col.*, 1934, 65.

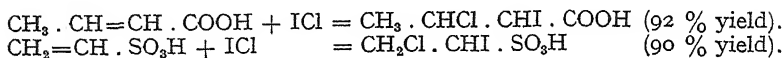
(1) Experiments³ in which pairs of olefins could compete for a limited supply of bromine in methylene chloride solution at -35° or -78° (in absence of light) showed that bromine addition was accelerated by the presence of electron repelling groups in the olefinic molecule and retarded by electron attracting groups. Some relative rates for bromine addition are given in Table I.

TABLE I.

Compound	$\text{CMe}_2=\text{CMe}_2$	$\text{CHMe}=\text{CH}_2$	$\text{CH}_2=\text{CH}_2$	$\text{CHMe}=\text{CHCOOH}$	$\text{CHBr}=\text{CH}_2$
Rel. rate	14.0	2.03	1	0.26	Small.

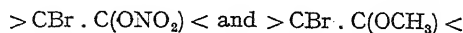
(2) In the addition of iodine chloride,⁴ the more positive iodine attaches itself to the negatively polarised carbon atom.

Thus,



(3) The double bond is most readily halogenated when situated in an *anion*. In aqueous solution, the maleate and fumarate ions add on chlorine at far greater speeds than do the undissociated acids; and this is true whether the reaction goes principally to halogenohydrin,⁵ or, in the presence of sufficient halide ion, to dihalogenide.⁶ Retardation by H^+ ion of the thermal bromination of maleic and fumaric acids in aqueous solution (with Br^- ion present)⁷ is interpreted to mean that the acid maleate and fumarate ions are, respectively, 140 times and 32 times as reactive as their parent acids. The completely dissociated ions are thought to be still more reactive. Similarly, velocity coefficients for the bromination of acrylic acid and sodium acrylate, in water, are about 30 and 9000 respectively.⁸ It is also stated⁸ that the allyl group, which adds bromine rapidly when in a neutral molecule, is unreactive in a positive ammonium ion.

(4) When olefinic halogenation takes place in a medium which can supply *anions*, these may attach themselves to one carbon atom of the double bond. Such reactions are considered more fully later, but a particularly significant example is the formation of the compounds* $\text{CH}_2\text{Br} \cdot \text{CH}_2\text{Cl}$, $\text{CH}_2\text{Br} \cdot \text{CH}_2\text{I}$, $\text{CH}_2\text{Br} \cdot \text{CH}_2\text{ONO}_2$, when ethylene is treated with bromine water containing sodium chloride, iodide and nitrate respectively.⁹ Anions can compete for attachment to the second carbon atom of the double bond; it follows that positive halogen initiates the attack, at the first unsaturated carbon atom. This is further shown by the preparation¹⁰ of compounds of the form $>\text{Cl} \cdot \text{C}(\text{OCH}_3) <$ by means of iodine nitrate, $\text{I} \cdot \text{NO}_3$, in methyl alcohol; and of the forms



by using bromine nitrate, $\text{Br} \cdot \text{NO}_3$, in chloroform and methyl alcohol respectively.

³ C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 1931, 2354; Anantakrishnan and Ingold, *ibid.*, 1935, 984, 1396.

⁴ Ingold and Smith, *ibid.*, 1931, 2742.

⁵ Read and Reid, *ibid.*, 1928, 745.

⁶ Terry and Eichelberger, *J. Amer. Chem. Soc.*, 1925, 47, 1067.

⁷ Berthoud and Mosset, *J. Chim. Physique*, 1936, 33, 272.

⁸ Robertson, Clare, McNaught and Paul, *J. Chem. Soc.*, 1937, 335.

* It must be observed that, owing to difficulties of isolation, the identification of these products, though extremely plausible, lacks the ultimate confirmation which would be furnished by conclusive analyses.

⁹ Francis, *J. Amer. Chem. Soc.*, 1925, 47, 2340.

(5) Further confirmation is evident in reactions, referred to at the end of this paper, in which addition at a double bond is initiated by positive halogen derived from compounds such as trinitro-bromo-methane.

Reviewing the evidence, it seems very probable that the vital condition for halogen addition is the attachment of positively polarised halogen to negative carbon. It remains for kinetic studies to determine how the halogen achieves this step and how subsequent steps complete the addition process.

Gaseous Halogenation.

The first appeal is to gas-phase kinetics; but the gaseous (thermal) additions of bromine and chlorine to ethylene are well known to be surface reactions at ordinary temperatures,¹⁰ proceeding at rates which are greatly influenced by the polar nature of the surface,¹¹ and having complex kinetics involving adsorbed water.¹² Chlorine addition is further complicated by induced substitution of ethylene dichloride.¹³ The gaseous additions of iodine to ethylene¹⁴ and of bromine to butadiene¹⁵ are also heterogeneous.

Bromination Experiments at High Temperatures.

Since these surface additions frequently have rates which diminish with rise of temperature,^{12, 15} there remains the possibility of studying a homogeneous addition reaction at a high temperature. This possibility is particularly attractive, since quantal calculations¹⁶ have suggested that bromine addition to the double bond may require an activation energy of about 25,000 cal., which would imply that homogeneous addition should be measurable at 300° C.

Some experiments * to test this point are illustrated in the diagram. The reaction is the bromination of vinyl bromide. Between 0° and 50° bromine adds to the double bond of vinyl bromide as a third order surface reaction, accelerated by moisture and retarded by rise of temperature.¹⁷ In the experiments shown in the diagram, bromine and vinyl bromide were enclosed in a glass bulb, placed in a furnace at 300°, with exclusion of light. Pressure changes were read on a Bourdon gauge. For complete addition to the double bond, the pressure should fall to the level indicated by the broken horizontal line; but in fact, after a small initial fall, the pressure remains constant, showing the absence of homogeneous bromine addition. Reaction mixtures, frozen out after heating for different times, were analysed; and hydrogen bromide was proved to be formed during the constant pressure stage, to an extent increasing with the time of heating. The calculated partial pressures of hydrogen bromide formed in different experiments are indicated by crossed circles in the diagram. Vinyl bromide does not decompose by itself at 300°. Pressure-time curves of a

^{9a} Uschakow and Tchistow, *Ber.*, 1935, 68, 824.

¹⁰ Stewart and Edlund, *J. Amer. Chem. Soc.*, 1923, 45, 1014; Stewart and Fowler, *ibid.*, 1926, 48, 1187.

¹¹ Norrish, *J. Chem. Soc.*, 1923, 123, 3006; Norrish and Jones, *ibid.*, 1926, 55.

¹² G. Williams, *ibid.*, 1932, 1747, 1758.

¹³ Stewart and Smith, *J. Amer. Chem. Soc.*, 1929, 51, 3082; 1930, 52, 2869.

¹⁴ Mooney and Reid, *J. Chem. Soc.*, 1931, 2597.

¹⁵ Heisig and Wilson, *J. Amer. Chem. Soc.*, 1935, 57, 859; Heisig and Davis, *ibid.*, 1936, 58, 1095.

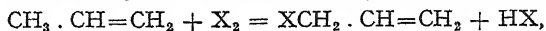
¹⁶ Sherman, Quimby and Sutherland, *J. Chem. Physics*, 1936, 4, 732.

* These experiments were carried out some years ago in the Laboratory of Colloid Science, Cambridge.

¹⁷ G. Williams, *Trans. Faraday Soc.*, 1938, 34, 1144.

similar character were obtained with bromine-ethylene mixtures at temperatures slightly above 300°.

Although these experiments are only of a preliminary nature, they suggest that suppression of surface addition at high temperature makes way for a *substitution* reaction rather than for homogeneous addition. This conclusion is in accord with recent results of flow experiments,¹⁸ which show that the principal reaction in the chlorination and bromination of propylene between 300° and 600° is that given by the equation



where X_2 is the halogen molecule.

Addition to the double bond was reduced to a minute fraction of the total reaction, and it was shown that the addition compound was not an intermediate in the formation of the substitution product. Further evidence on this point is furnished by a comparison of the products of

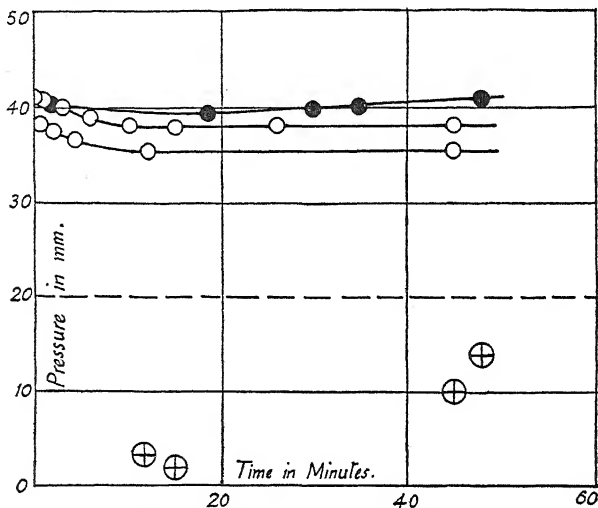


FIG. 1.—Bromination of vinyl bromide at 300° C.
⊕ Partial pressure of HBr formed.

chlorination of ethylene at different temperatures. At 20°, in pyrex tubes, a 33 % yield of ethylene dichloride is accompanied by 60 % of tri- and tetra-chloroethanes—substitution products of ethylene dichloride—formed by an “induced” substitution dependent on preliminary addition.^{18, 19} On the other hand, above 300° the principal chlorination product of ethylene is vinyl chloride.¹⁸

Since these reactions have not been proved to be homogeneous, the discovery of preferential substitution of olefins at high temperatures does not at once invalidate quantal arguments¹⁶ to the effect that homogeneous bromine addition should proceed far more easily than substitution. At the same time, these arguments receive no experimental support. The upshot of this discussion must be that no experimental conditions have yet been realised, which permit halogen addition at a double bond to proceed through the union of isolated halogen and olefin molecules, meeting in binary collision.

¹⁸ Groll and Hearne, *Ind. Eng. Chem.*, 1939, 31, 1530; McBee and Hass, *ibid.*, 1941, 33, 137; Burgin, Hearne and Rust, *ibid.*, 385.

¹⁹ Groll, Hearne, Rust and Vaughan, *ibid.*, 1939, 31, 1239.

Halogen Addition in Solution.

Much the same picture is presented by halogenation in solution; saturation of the double bond is achieved through devious modes of attack, among which the following may be distinguished:—

- (1) Attack by halogen atoms.
- (2) Two-stage addition by halogen molecules.
- (3) Heterogeneous mechanisms.

Photo-halogenation—Attack by Halogen Atoms.

It is useful, in the first place, to consider photo-addition of halogens in the gas phase; and a number of gaseous photo-additions are listed in Table II. The high quantum efficiencies prove them to be chain reactions

TABLE II.—GASEOUS PHOTO-ADDITION.

Reaction.	Temp. °C.	Wave-length, Å.	Quantum Efficiency.	Effect of Oxygen.
I. ²¹ $\text{Cl}_2 + \text{H}_2\text{C} : \text{CH}_2$	25°	4360	(large)	—
II. ²² $\text{Cl}_2 + \text{ClHC} : \text{CHCl}$ trans-	80-95°	4360	7000	O ₂ retards. No oxidation.
III. ²² $\text{Cl}_2 + \text{ClHC} : \text{CHCl}$ cis-	95°	4360	7000	O ₂ retards. No oxidation.
IV. ²² $\text{Cl}_2 + \text{ClHC} : \text{CCl}_2$	80-115°	4360	700	O ₂ inhibits and oxidises.
V. ²³ $\text{Cl}_2 + \text{Cl}_2\text{C} : \text{CCl}_2$	40° or below.	4358	453 max.	O ₂ inhibits and oxidises.
VI. ²² $\text{Br}_2 + \text{ClHC} : \text{CHCl}$ trans-	90-130°	5460	1100	—

II and III. Rates of reaction at 95° identical.

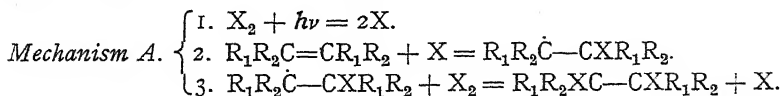
IV. Sensitised oxidation ²⁴ gives $\text{CCl}_3\text{H} \cdot \text{COCl}$.

V. Sensitised oxidation ²³ gives $\text{CCl}_3 \cdot \text{COCl}$ (90 %) and COCl_2 (10 %).

and, except I, their rates are all given by the equation

$$-d[\text{X}_2]/dt = k \cdot I_{\text{abs}} \cdot [\text{X}_2] \quad (1)$$

or, as in VI, by variants of this equation required only to take account of special chain-termination processes. In all, the chain-initiation and chain-propagation steps are thought to be ²⁰



This is the simplest mechanism which fits the facts, but it has been pointed out ²³ that the experimental relations for V. can also be interpreted by a mechanism involving attack on the double bond by Cl_3 , an

²⁰ Schumacher, *Angew. Chem.*, 1936, 49, 613; Müller and Schumacher, *Z. Elektrochem.*, 1937, 43, 807.

²¹ Stewart and Weidenbaum, *J. Amer. Chem. Soc.*, 1935, 57, 2036.

²² Müller and Schumacher, *Z. physikal. Chem., B.*, 1937, 35, 285, 455; 1939, 42, 327.

²³ Dickinson and Carrico, *J. Amer. Chem. Soc.*, 1934, 56, 1473.

²⁴ Müller and Schumacher, *Z. physikal. Chem., B.*, 1937, 37, 365.

entity which has been calculated to be stable at room temperature;²⁵ and attack by Br_2 has been proposed²⁶ in VI. But the triatomic halogen mechanism is not demanded by the experimental results,²⁰ and it seems safer to adopt the atomic mechanism A., especially for the reactions occurring at higher temperatures. In all these reactions, the energy of activation for step A.2 is estimated to be practically zero, and it is shown experimentally to be very small in I.²¹ For step A.3, the activation energy is estimated to be 11, 5.3 and 3.1 k.cal. in reactions VI, IV and II respectively.

As shown in Table II, oxygen retards photo-addition, either by removal of chain-carriers or, in other instances, through replacement of halogenation by halogen-sensitised photo-oxidation, itself a chain reaction.

The gaseous photo-additions may now be compared with those occurring in solution. In carbon tetrachloride solution, photo-bromination²⁷ of the compounds $\text{C}_6\text{H}_5 \cdot \text{CH}=\text{CH} \cdot \text{COOH}$, $\text{C}_6\text{H}_5 \cdot \text{CH}=\text{CH} \cdot \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5 \cdot \text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{CN}$, $m\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}=\text{C}(\text{COOC}_2\text{H}_5)_2$ have been found to follow equation (1) above. They are chain reactions (having quantum efficiencies up to 36), and the above mechanism A. has been attributed to them, as also to the photo-bromination of tetrachloroethylene,³¹ to the chlorination of tetrachloroethylene,²⁸ and of cinnamic acid,²⁹ and to the iodination of ethylene,³⁰ and of allyl alcohol,⁷ all in carbon tetrachloride solution. The photo-chlorination of tetrachloroethylene has almost the same rate in solution as in the gas phase. The photo-bromination of the substance $\text{C}_6\text{H}_5 \cdot \text{CH}=\text{C}(\text{C}_6\text{H}_5) \cdot \text{COOH}$ is complicated by side reactions, and does not follow the same rate law.³²

In opposition to the atomic mechanism, it has been argued³³ that free bromine atoms are unlikely to survive in solution; and other mechanisms B and C have been proposed for photo-additions.

Mechanism B.

1. $\text{Br}_2 + h\nu = 2 \text{ Br} \cdot$
2. $\text{Br} \cdot + \text{Br}_2 = \text{Br}_3 \cdot$
3. $\text{A} + \text{Br}_3 \cdot = \text{ABr}_2 + \text{Br} \cdot$

Mechanism C.

1. $\text{Br}_2 + h\nu = \text{Br}_2^* \cdot$
2. $\text{A} + \text{Br}_2^* \cdot = \text{ABr}_2^* \cdot$
3. $\text{ABr}_2^* \cdot + \text{Br}_2 = \text{ABr}_2 + \text{Br}_2^* \cdot$

Mechanism B has been suggested for the bromination of cinnamic acid and stilbene in carbon tetrachloride and carbon disulphide,³⁴ and mechanism C for the bromination of cinnamic acid in carbon tetrachloride.³⁵ On the other hand, calculations³⁶ have suggested that Br_3 would be less reactive than Br_2 towards the double bond. It also seems questionable whether the excited $\text{Br}_2^* \cdot$ molecule would add to the double

²⁵ Rollefson and Eyring, *J. Amer. Chem. Soc.*, 1932, **54**, 176.

²⁶ J. C. Ghosh, S. K. and S. C. Bhattacharyya, *Z. physikal. Chem.*, B., 1936, **32**, 145.

²⁷ Berthoud and Béraneck, *J. Chim. physique*, 1927, **24**, 213; Berthoud and Nicolet, *ibid.*, 1928, **25**, 40; also ref. 7.

²⁸ Dickinson and Leermakers, *J. Amer. Chem. Soc.*, 1932, **54**, 3852, 4648.

²⁹ Berthoud and Porret, *Helv. Chim. Acta.*, 1934, **17**, 237.

³⁰ Schumacher and Wiig, *J. Amer. Chem. Soc.*, 1930, **52**, 3132; *Z. physikal. Chem.*, B., 1930, **11**, 45.

³¹ Willard and Daniels, *J. Amer. Chem. Soc.*, 1935, **57**, 2240.

³² Berthoud and Porret, *J. Chim. physique*, 1934, **17**, 1548.

³³ Franck and Rabinowitsch, *Trans. Faraday Soc.*, 1934, **30**, 120.

³⁴ Purkayastha and Ghosh, *J. Indian Chem. Soc.*, 1927, **4**, 409, 553.

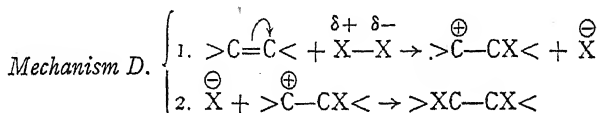
³⁵ Bauer and Daniels, *J. Amer. Chem. Soc.*, 1934, **56**, 378, 2014.

³⁶ Sherman and Sun, *ibid.*, 1936.

bond in one step, as shown in C. Bearing in mind the gas-phase results, it seems highly probable that stepwise addition by means of halogen atoms and ABr radicals is a possible mechanism for photo-addition in solution. This mechanism has obvious analogies to those found in thermal reactions.

Thermal Addition in Solution—Two-stage Addition.

Initiation by chlorine or bromine atoms in thermal reactions at ordinary temperatures can scarcely be contemplated; and it is necessary to seek for ionic or molecular mechanisms. From the kinetic point of view, a sharp distinction must be drawn between the addition reaction in dissociating solvents and that in non-dissociating solvents. In the former, halogen addition is definitely a two-stage process, which may be formulated, in the extreme case of a strongly dissociating solvent,



General evidence for addition in two stages is afforded by the occurrence of trans-addition of chlorine or bromine,³⁷ both in aqueous solution,³⁸ and in a non-hydroxylic solvent, such as ether.³⁹ Particular evidence, for dissociating solvents, is furnished by the fact, referred to earlier,

TABLE III.

Medium.	Competing Anion.	Reactants.	Product.
VII. ⁴⁰ H ₂ O VIII. ^{5,41} H ₂ O	OH' OH'	Br ₂ + CH ₂ :CH ₂ Br ₂ + CH ₃ CH:CHCOOH	CH ₂ Br . CH ₂ OH (75 %). CH ₃ CHOH . CHBrCOOH (100 %).
IX. ⁴² H ₂ O X. ⁹ H ₂ O + NaCl XI. ⁹ H ₂ O + NaI XII. ⁹ H ₂ O + NaNO ₃ XIII. ⁴³ CH ₃ COOH XIV. ⁴⁴ (CH ₃ CO) ₂ O	OH' Cl' I' NO ₃ ' CH ₃ COO' (CH ₃ COO)	Cl ₂ + CH ₂ :CH ₂ Br ₂ + CH ₂ :CH ₂ Br ₂ + CH ₂ :CH ₂ Br ₂ + CH ₂ :CH ₂ Cl ₂ + CH ₂ :CH ₂ Cl ₂ + CH ₂ :CH ₂	CH ₂ Cl . CH ₂ OH CH ₂ Br . CH ₂ Cl CH ₂ Br . CH ₂ I CH ₂ Br . CH ₂ NO ₃ CH ₂ Cl . CH ₂ OCOCH ₃ CH ₂ Cl : CH ₂ OCOCH ₃ (17 %).
XV. ⁴⁴ CH ₃ COOCH ₃	(CH ₃ COO)	Cl ₂ + CH ₂ :CH ₂	CH ₂ Cl . CH ₂ OCOCH ₃ (30 %).
XVI. ⁴⁵ CH ₃ COOH XVII. ⁴⁶ CH ₃ OH	CH ₃ COO' (CH ₃ O)	Cl ₂ + CH ₂ ClCH:CH ₂ Br ₂ + C ₆ H ₅ CH:CHC ₆ H ₅	CH ₂ ClCHCl . CH ₂ OCOCH ₃ C ₆ H ₅ CHBr . CH(OCH ₃)C ₆ H ₅ (99 %).

³⁷ E.g. Michael, *J. pr. Chem.*, 1895, (ii), 52, 352; Frankland, *J. Chem. Soc.*, 1912, 101, 654.

³⁸ Lossen, *Annalen*, 1906, 348, 261; Kuhn and Ebel, *Ber.*, 1925, 58, 919; Kuhn and Wagner-Jauregg, *ibid.*, 1928, 61, 504.

³⁹ McKenzie, *J. Chem. Soc.*, 1912, 101, 1196.

⁴⁰ J. Read and M. M. Williams, *ibid.*, 1920, 117, 359.

⁴¹ Billmann, *Rec. Trav. chim.*, 1917, 36, 313.

⁴² Gomberg, *J. Amer. Chem. Soc.*, 1919, 41, 1414. Cf. Moureu and Dodé, *Bull. Soc. chim.*, 1937, (v), 4, 281.

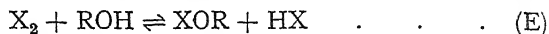
⁴³ Backer and Strating, *Rec. Trav. chim.*, 1934, 53, 525.

⁴⁴ Weber, Hennion and Vogt, *J. Amer. Chem. Soc.*, 1939, 61, 1457.

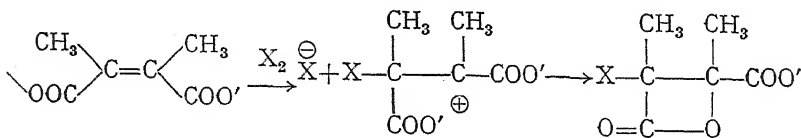
⁴⁵ Bockemüller and Hoffmann, *Annalen*, 1935, 519, 165.

⁴⁶ Bartlett and Tarbell, *J. Amer. Chem. Soc.*, 1936, 58, 466.

that anions from the reaction medium can compete in step D.2 with halide ion, so that addition products with mixed addenda are formed. Examples of this behaviour are summarised in Table III, and the reactions may be supposed to take place by the mechanism D. It must be recalled, however, that halogens enter into equilibria of the type



and, by addition of silver nitrate to remove HX, solutions of hypobromous acid in water, of acyl hypohalogenites $XO \cdot CO \cdot R$ in carbon tetrachloride,⁴⁵ and of methyl hypobromite $BrOCH_3$ in methyl alcohol⁴⁷ can be obtained. These solutions show additivity towards the double bond, which may be ascribed to the molecule XOR, especially in a solvent such as carbon tetrachloride. It has been supposed, therefore, that the products shown in Table III were formed through establishment of equilibria of type E, followed by addition of XOR to the double bond. When the starting material is a solution of halogen in a hydroxylic solvent, it is to some extent academic to enquire whether step D.2 is completed by addition of a competing anion derived from the "environment" or from a molecule XOR, because addition of XOR to the double bond may itself be supposed to occur by a two-stage process analogous to mechanism D.⁴⁸ However, kinetic evidence exists in support of the view that the competing anion does not necessarily come from the molecule XOR. Thus in the bromination of stilbene in methyl alcohol⁴⁶ (reaction XVII), the rate of reaction and the proportional yield of methoxybromide are independent of H^+ ion concentration, although, in the equilibrium E the concentration of $BrOCH_3$ obviously depends on the H^+ ion concentration. Moreover, the influence of added Br^- ion (a) in retarding reaction, and (b) in lowering the relative amount of methoxybromide in the product, can be quantitatively accounted for, the first by supposing that Br_2 and Br_3^- ion both react in step D.1 (rate of attack by $Br_3^- = 0.01$ of that by Br_2), and the second by supposing that Br^- ion and CH_3OH compete in step D.2. In halogenation by chlorine or bromine water also, the proportion of halogenohydrin formed is depressed by addition of halide ion,^{6, 41} but unaffected by acid;^{9, 41} and in this reaction the matter is clinched by the isolation of lactones,⁴⁹ formed on treating sodium dimethylmaleate and dimethylfumarate with chlorine or bromine water, by the mechanism



as is proved by the impossibility of obtaining the lactones from the halogenohydrins or other conceivable intermediate addition compounds.

The equilibria E seem, therefore, to be largely irrelevant in the addition of halogens in dissociating solvents; and the kinetic evidence justifies the presentation of the competition reactions of Table III as evidence that halogenation in such solvents proceeds by the two-stage

⁴⁷ Meinel, *Annalen*, 1934, **510**, 129; 1935, **516**, 231.

⁴⁸ E.g. Robinson, "Outline of an Electrochemical Theory of the Course of Organic Reactions," *Inst. of Chem.*, 1932.

⁴⁹ Tarbell and Bartlett, *J. Amer. Chem. Soc.*, 1937, **59**, 407.

Kinetics of Halogen Addition in Solution.

Early work^{1, 54} on the rates of halogen addition to double bonds relates mainly to non-dissociating solvents, where particularly complex phenomena abound. In dissociating solvents, on the other hand, consistent and intelligible relationships are found, as is shown in Table IV.

TABLE IV.—THERMAL HALOGEN ADDITION IN DISSOCIATING SOLVENTS.

Solvent.	Temp.	Halo- gen.	Unsat. Comp. A.	Conc. M.	E. k.cal.	Rate equal to:
1. ⁷ Water + KCl + H·	25°	Br ₂	Maleic acid Fumaric acid	A. 0.0086 — 0.0172 Br ₂ 0.00075 — 0.003	— —	$k_2[A][Br_2]$
2. ⁷ Water + KI	0-30°	I ₂	Allyl alcohol	A. 0.1-0.2 I ₂ 0.00025 — 0.01	(17.6)	$k_2[A][I_2]$
3. ⁴⁶ MeOH + KBr	0°	Br ₂	Stilbene	—	—	$k_2[A][Br_2]$
4. ⁵⁵ Acetic acid	25°	Cl ₂	<i>cis</i> -Cinnamic acid	0.05 — 0.00625	—	$k_2[A][Cl_2]$
5. ⁵⁵ Acetic acid	25-55°	I ₂	Allyl alcohol	A. 0.5 I ₂ 0.02	4.8	$k_3[A][I_2]^2$
6. ⁵⁵ Nitro- benzene	14-45°	I ₂	Allyl alcohol	A. 0.5-0.25 I ₂ 0.02-0.01	3.3	$k_3[A][I_2]^2$
7. ⁵⁵ Acetic acid	25°	ICl	Allyl acetate	0.025 — 0.0125	—	$k_3[A][ICl]^2$
8. ⁵⁵ Acetic acid	25°	ICl	Acrylic acid	0.05 — 0.0125	—	$k_3[A][ICl]^2$
9. ⁵⁵ Acetic acid	25°	BrCl	<i>cis</i> -Cinnamic acid	—	—	$k_3[A][BrCl]^2$
10. ⁸ Acetic acid	25-50°	Br ₂	<i>cis</i> -Cinnamic acid	0.025 — 0.0125	5.8	$k_3[A][Br_2]^2$
11. ⁸ Acetic acid + 25 % H ₂ O + N/4 H ₂ SO ₄	0-25°	Br ₂	<i>cis</i> -Cinnamic acid	0.0125 — 0.00625	8.5	$k_2[A][Br_2]$
12. ⁸ Acetic acid	25-50°	Br ₂	Allyl acetate	0.025	2.7	$k_3[A][Br_2]^2$
13. ⁵⁵ Acetic acid	17-40°	Br ₂	Allyl acetate	0.001 — 0.0003	9.0	$k_2[A][Br_2]$

The concentrations give the range over which the reaction order was tested. Unless otherwise stated, halogen and olefinic compound were present in equal concentrations. In reactions 1-3, the rate expressions only hold for constant halide ion concentration (in 1 for const. H· ion conc. as well) because both X₂ molecule and X₃' ion react.

⁵⁴ E.g. Bauer, *Ber.*, 1904, 37, 3317; Plotnikov, *Z. physikal. Chem.*, 1905, 53, 605; Herz and Mylius, *Ber.*, 1906, 39, 3816; Herz and Rathmann, *ibid.*, 1913, 46, 2588.

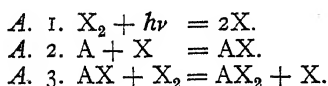
This table is constructed mainly from the results of Berthoud,⁷ and of P. W. Robertson and co-workers.^{8, 55} In the examples listed, light was rigidly excluded; and the reaction order was deduced from experiments in which the *initial concentrations* of the reactants were varied. This is essential in reactions of this kind, in which constancy of velocity coefficients through the course of individual halogenations may be distorted—or simulated—by secondary effects.

Dissociating Solvents.

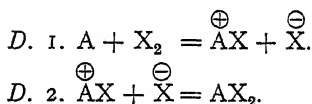
The reactions collected in Table IV are homogeneous, reproducible and insensitive to stray catalysts. The noteworthy result is that, for Br₂, I₂ and mixed halogens, addition is a *second order* reaction in water or methyl alcohol (1-3), but a *third order* reaction in acetic acid or nitrobenzene (5-10). Chlorination is second order even in acetic acid (4). Further, a reaction (10) which is third order in acetic acid becomes second order (11) in the presence of 25 % water. The same change of order is achieved by drastic lowering of reactant concentrations in acetic acid (12 and 13). As would be anticipated, the third order reaction invariably has a much lower activation energy than the second order reaction (*cf.* especially the pairs 10-11 and 12-13).

Combining the photo-chemical results with those of Table IV, the kinetics of halogen addition may be represented formally by the following schemes, in which A represents the olefinic molecule and X₂ the halogen molecule.

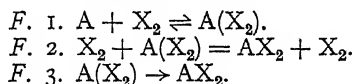
A. (Photo-addition).



D. (Thermal—in water).



F. (Thermal—in acetic acid).



In photo-addition, step A.3 determines the rate of reaction. In thermal addition the rate will be determined by D.1 in water, and by either F. 2 or F. 3 in acetic acid. The corresponding equations for the rate of addition will be

$$\text{Ionic mechanism D.} \quad -d[X_2]/dt = k_2 \cdot [A][X_2] \quad (2)$$

$$\text{Molecular mechanism F. (1 + 2)} \quad -d[X_2]/dt = k_3 \cdot [A][X_2]^2 \quad (3)$$

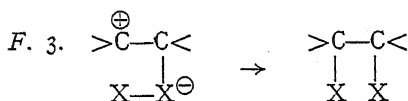
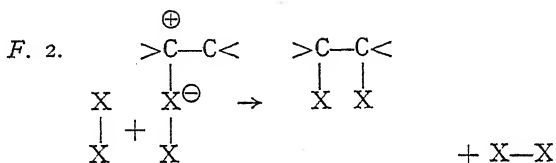
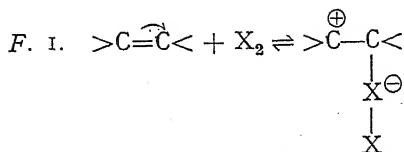
$$\text{Molecular mechanism F. (1 + 3)} \quad -d[X_2]/dt = k_2 \cdot [A][X_2] \quad (4)$$

Mechanisms A and D are those postulated previously for photo-addition, and for thermal addition in a strongly dissociating solvent. In mechanism F, A(X₂) is thought to be a complex formed reversibly. The complex gives the normal addition compound AX₂ after collision with a further X₂ molecule (step F.2; *cf.* reaction 12), or it may rearrange to give AX₂ (step F.3). The latter process only becomes evident when the concentration of X₂ is very low (reaction 13), so that the chance of what

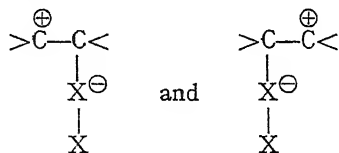
⁵⁵ Bythell and Robertson, *J. Chem. Soc.*, 1938, 179; White and Robertson, *ibid.*, 1939, 1509; Walker and Robertson, *ibid.*, 1515.

amounts to a three-body collision $A + 2X_2$ is greatly reduced. In slightly different words, we might say that $A(X_2)$ is formed by collision of A with X_2 and may re-dissociate into A and X_2 . But on rare occasions it may rearrange to give AX_2 and if, during its lifetime, it is fortunate enough to collide with a further X_2 molecule, it can form AX_2 by a process requiring less activation energy.

As regards the structural plausibility of these molecular entities, mechanism D has already been formulated, and mechanism F would be written



The formation of the complex would be dependent on the capacity of Br and I atoms to expand their outer ring of electrons.⁵⁵ Such complexes, in which the double bond acts as an electron donor, have been proposed to explain the formation of co-ordination compounds by olefins.⁵⁶ The possibility of resonance between



amounts virtually to a three-member ring, a view advanced⁵⁷ for the organic radical formed in step D.1 in order to provide stereo-chemical stability and to account for the fact that, for example, maleic and fumaric acids give different bromine addition products. The photo-chemical radical (formed in step A.1) has one more electron than the thermal radical; interconversion of geometrical isomers is brought about, under the influence of light, by halogen atoms.⁵⁸

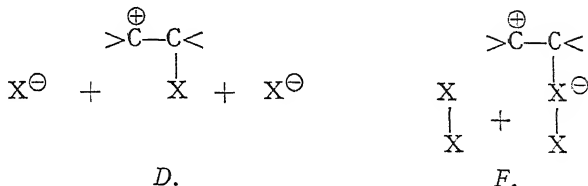
Chlorine does not add by mechanism F, because it is reluctant to expand its outer shell, and because it forms halide anion more easily than bromine or iodine. The essential difference between mechanisms

⁵⁶ Bennett and Willis, *J. Chem. Soc.*, 1929, 256; Winstein and Lucas, *J. Amer. Chem. Soc.*, 1938, 60, 836; cf. Meisenheimer, *Annalen*, 1927, 456, 126.

⁵⁷ Roberts and Kimball, *J. Amer. Chem. Soc.*, 1937, 59, 947.

⁵⁸ E.g. Berthoud, *Trans. Faraday Soc.*, 1926, 21, 554; Schmidt, *Z. physikal. Chem., B.*, 1928, 1, 205; Kharasch, Mansfield and Mayo, *J. Amer. Chem. Soc.*, 1937, 59, 1155.

D and F seems to be that, in water, the positive organic radical and halide ion are produced in step D.1; whereas, in acetic acid or nitrobenzene, the initially attacking halogen does not readily split off halide ion in step F.1.¹ The situations existing when step 1 has been completed and step 2 is beginning may be represented



If it is considered that the successful accomplishment of the addition process may depend upon the steps 1 and 2 being almost simultaneous in time (*cf.* co-ordinative mechanism, p. 757), then the failure to split off halide ion in step F.1 demands the triple collision mechanism, assuming—as the evidence suggests—that halogen and olefin do not usually unite to the stable addition compound in one binary collision. Addition of halogens by second order reaction may thus be associated with the ionic mechanism, and addition by third order reaction with a molecular mechanism. The same distinction may perhaps be applied to the competition reactions of Table III; and it may be noted that van't Hoff⁵⁹ found the bromination of fumaric acid in water (which gives bromohydrin⁴¹) to be nearly second order; whilst the bromination of undecenoic acid in acetic acid is third order, and gives 30 % of bromoacetoxy derivative.⁸

Although the reactions in acetic acid collected in Table IV fall into a consistent scheme, there are other brominations in this medium which do not. An apparent instance of catalysis by hydrogen bromide in the bromination of cinnamic acid in acetic acid⁶⁰ is really due to catalysis by HBr of stereo-conversion during bromination.⁸ Nevertheless, the brominations of vinyl bromide and acrylic acid in acetic acid display induction periods and sensitivity to catalysis by HBr,⁸ behaviour more commonly associated with addition in non-hydroxylic solvents. Bromine addition to tiglic acid in acetic acid may also have a more complex mechanism.⁶¹

Non-dissociating Solvents—Catalytic and Heterogeneous Mechanisms.

In solvents such as carbon tetrachloride or chloroform, halogen additions tend to have less reproducible rates and induction periods may be observed.¹ Hydrogen bromide and hydrogen iodide catalyse bromination⁶² and iodination⁷ respectively; moisture may accelerate⁶³ and oxygen inhibit.⁵³ The results are not sufficiently advanced for detailed discussion; but a partial clue may lie in the discovery⁸ that bromine addition in carbon tetrachloride is accelerated by packing the solution

⁵⁹ Van't Hoff, *Studies in Chemical Dynamics*, 1896.

⁶⁰ D. M. Williams, *J. Chem. Soc.*, 1932, 979.

⁶¹ Anantakrishnan and Venkataraman, *ibid.*, 1939, 224.

⁶² Ref. 1; also: N. W. Hanson and T. C. James, *J. Chem. Soc.*, 1928, 1955; Hanson and D. M. Williams, *ibid.*, 1930, 1059; Williams, *ibid.*, 1932, 2911.

⁶³ Davis, *J. Amer. Chem. Soc.*, 1928, 50, 2769.

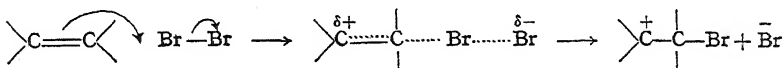
The addition of nucleophilic addenda can be represented along similar lines, but successful polarisation will result from conditions which are the converse of those indicated by Table I.⁶⁷

University of London,
King's College.

⁶⁷ Cf. Watson, *Modern Theories of Organic Chemistry*, Oxford, 1937.

GENERAL DISCUSSION

Dr. E. D. Hughes (*London-Aberystwyth*) said: In the rate-determining stage of halogen-addition, formally neutral reactants give rise to a partial separation of charges in the transition state, *e.g.*,



and the reaction may be expected to be facilitated by a polar environment. If the addition is carried out in a polar solvent, the stabilisation of the transition state is achieved by the interaction of its quasi-ionic charges with solvent dipoles; but this is not possible when a non-polar solvent is employed, and it is in the latter circumstances that surface catalysis and catalysis by hydrogen bromide, etc., become apparent.

The evidence in favour of a mechanism in which the initiation of the addition is by positively polarised halogen seems particularly well founded. The preference expressed by some authors¹ for the alternative hypothesis (attack by negative halogen) is based largely on a misinterpretation of the stereochemical data, which are, in fact, entirely consistent with the conventional view.²

Dr. W. A. Waters (*Durham*) said: Many of the anomalous kinetic observations concerning the halogenation of olefines in solvents such as carbon tetrachloride, benzene and carbon disulphide, and in particular the concurrent oxygen absorption, seem to be explicable on the hypothesis that these reactions involved neutral atoms and free radicals. Considerations dealt with in the general review of solvent influences in free radical reactions³ would be of significance in this connection, and obviously the kinetics of these addition reactions must be highly complicated.

¹ Cf. Ogg, *J. Amer. Chem. Soc.*, 1935, **57**, 2727; *ibid.*, 1939, **61**, 1946.

² Roberts and Kimball, *ibid.*, 1937, **59**, 947.

³ Waters, *This vol.*, p. 780.

THE MECHANISM OF THE FRIEDEL-CRAFTS REACTION.

BY FRED FAIRBROTHER.

Received 10th September, 1941.

The term "Friedel-Crafts reaction" is used in its widest sense to cover a variety of different reactions which have been developed since the first investigations of C. Friedel and J. Crafts in 1877 on the alkylation and acylation of benzene.

Much experimental work is still required before a complete picture can be given of the mechanism of all types of the reaction, but there is now good evidence to show that in the case of alkylations and acylations

by the use of a metal halide catalyst and the appropriate organic halide, an initial and necessary step in the reaction is the transition of the mainly covalent carbon-halogen bond of the alkyl or acyl halide, into an ionic bond, *i.e.*, the ionisation of the compound, as distinct from electrolytic dissociation, which may then follow if the dielectric constant of the solution is sufficiently high. The energy required to bring about this step is supplied mainly by the energy of formation of a complex metal anion, and to a less extent by the increased energy of solvation of the resulting ionic pair.

The view that some kind of double compound is formed between the metal halide catalyst and one or other or both of the reactants, as a step in the reaction, has been generally held for a long time, and Perrier¹,² and Böeseken³,⁴ isolated crystalline compounds of aluminium chloride with acid chlorides. The fact, however, that some Friedel-Crafts reactions could be carried out with much less than the molecular proportion of aluminium chloride led Böeseken⁵ to suggest that the intermediate-compound theory should be replaced by a catalytic hypothesis, according to which the molecules were activated by the catalyst, combination then occurring between these activated molecules, with the evolution of hydrogen chloride. Later⁶ he suggested that the action of the aluminium chloride was due to a "dislocating influence" on the molecules, this influence being exerted where the molecule was weakest: "in organic chlorides it is probably the chlorine atom which is thus activated."

Meerwein⁷ and Hückel⁸ have suggested that the complexes which are formed are co-ordination compounds containing the complex anion $[AlCl_4]^-$, thus $CH_3 \cdot COCl + AlCl_3 \rightarrow (CH_3 \cdot CO)^+ + [AlCl_4]^-$.

Experimental evidence in support of a breaking of the covalent carbon-halogen bond, probably by such an ionisation process has been given by the study of the isotopic exchange of radioactive halogens between organic and inorganic halides. Thus, it was shown (Fairbrother⁹) that the hydrogen chloride liberated in the Friedel-Crafts reactions, using aluminium chloride, is in radioactive equilibrium with the latter, and also that an exchange of chlorine atoms takes place between the aluminium chloride and the organic chloride, even in the absence of a third component.

Further experiments, with a number of pairs of inorganic and organic bromides (Fairbrother¹⁰), showed that the ease of exchange of radiobromine was closely parallel to the reactivity in the Friedel-Crafts syntheses. For example, whilst aluminium bromide readily exchanges all its bromine atoms with those of most organic bromides, when simply dissolved in the latter or when both reactants are dissolved in carbon bisulphide, other catalysts like $SnBr_4$ or $SbBr_3$ only show a rapid exchange with the more reactive organic bromides. Bromobenzene is outstanding in the slowness of its exchange, even with aluminium bromide, which is consistent with the early observation of Friedel and Crafts¹¹

¹ Perrier, *Compt. rend.*, 1893, 116, 1298.

² Perrier, *Ber.*, 1900, 33, 815.

³ Böeseken, *Rec. trav. chim.*, 1900, 19, 19.

⁴ Böeseken, *ibid.*, 1901, 20, 102.

⁵ Böeseken, *ibid.*, 1904, 23, 1904.

⁶ Böeseken, *ibid.*, 1910, 29, 85.

⁷ Meerwein, *Annalen*, 1927, 455, 227.

⁸ Hückel, *Theoretische Grundlagen der Organischen Chemie*, 1931, vol. I, p. 351.

⁹ Fairbrother, *J. Chem. Soc.*, 1937, 503.

¹⁰ Fairbrother, *ibid.*, 1941, 293.

¹¹ Friedel and Crafts, *Compt. rend.*, 1877, 84, 1450.

that halogenobenzenes would not react in the same manner as alkyl halides. This work is being extended on a more quantitative basis, and the results (unpublished) so far obtained by the author and Mrs. E. L. Seymour, show that the rates of exchange under comparable conditions, of bromine, between stannic bromide and a series of alkyl bromides follow the sequence: ethyl < iso-propyl < n-propyl < sec-butyl < n-butyl < iso-butyl < tert-butyl, the rate of exchange with tert-butyl bromide at 25° being over 30 times faster than with ethyl bromide.

Wohl and Wertyporoch¹² have shown that aluminium bromide gives a conducting solution in ethyl bromide and that transference experiments indicate that the aluminium is in the anion, which is consistent with the present theory.

Preliminary measurements have now been made along a new line of attack on this problem. Aluminium bromide is freely soluble in cyclohexane, apparently without decomposition at ordinary temperatures. Measurements of the freezing-points and dielectric polarisabilities of dilute solutions of aluminium bromide in cyclohexane, show that the solute is present almost wholly as the dimer Al_2Br_6 , and that its dipole moment is zero, or very small. If to such a solution be added some bromobenzene, the polarisability of the resulting ternary mixture is very close to that of the sum of its components when measured apart, and the solution may be kept for several days with very little change in its dielectric constant. On the other hand, if ethyl bromide be used in place of bromobenzene, the apparent molar orientation polarisation of the aluminium bromide jumps from about zero to more than 300 c.c., corresponding to an apparent dipole moment of about 4 Debye units, and the solution only remains stable at 25° for an hour or so, after which it becomes turbid and feebly conducting, and some HBr is slowly evolved.

These results show that aluminium bromide in solution forms a highly polar complex compound with ethyl bromide, but not, under the same conditions, with bromobenzene, which again is in agreement with the exchange experiments and the behaviour of these compounds in the Friedel-Crafts reactions.

Experimental.

Cyclohexane: a commercial sample was shaken for 12 hours with concentrated sulphuric acid + 1 to 2 % SO_3 , then for several hours with sulphuric acid alone, washed, dried and fractionated. It was then dried for 6 days with phosphoric oxide and again distilled: B.p. $82.25^\circ \pm 0.02/763$ mm. Ethyl bromide and bromobenzene: commercially "pure" specimens were fractionated, dried over phosphoric oxide, and again fractionated. Aluminium bromide: Haen's "pro Synth." was freshly sublimed in small portions *in vacuo* at about 1μ Hg. immediately before the preparation of each solution and transferred to the solvents with only a few seconds exposure to the air.

The dielectric constants were measured at about 100 Kc. by means of a Muirhead Type 3 — A Heterodyne Capacity Meter. This instrument was first calibrated by the step by step method, for linearity of scale, at 50 points, using a $11\mu\text{F}$ fixed capacity air condenser. The capacities could be measured to $\pm 0.02 \mu\text{F}$, or about 1 part in 10,000 of the smallest capacity used, that of the dielectric cell filled with air. The solutions

¹² Wohl and Wertyporoch, *Ber.*, 1931, 64, 1357, 1369.

were measured in a 3-plate platinum-glass cell of about $215\mu\text{F}$ capacity, previously described (Fairbrother¹³).

The densities were measured in a glass capped Sprengel-type pycnometer of about 13 c.c. capacity. Both dielectric cell and pycnometer, were immersed in the same oil thermostat at $25^\circ \pm 0.01^\circ$. The dielectric cell was calibrated in the usual manner with dry benzene, assuming the dielectric constant of the latter to be 2.2727 at 25° (Hartshorn and Oliver¹⁴). The electron polarisability P_e was obtained from the refractive indices of the solutions measured at Hg_{5461} by a Pulfrich refractometer.

The results are given in the following table, in which f_2 is the mol. fraction of AlBr_3 (calculated as single molecules) and f_3 that of the bromobenzene or ethyl bromide respectively. The other symbols have their usual significance.

Discussion.

The average value of 45.4 c.c. for the molar polarisability of AlBr_3 , or 90.8 c.c. for the double molecule, is in good agreement with 44.8 c.c. given by Nespital¹⁵ for AlBr_3 in carbon bisulphide solution, and 90 c.c. given by Plotnikow, Scheka and Jankelewitsch¹⁶ for Al_2Br_6 , both molten and in solution in bromine and in carbon bisulphide.

The electron polarisability (Av. 32.5 c.c.) is in agreement with the figure of 32.8 c.c. calculated by Nespital¹⁷ from ionic radii; but whereas Nespital assumed an atom polarisability of 5.5 c.c., leading to a moment of 0.55 D., it seems more probable that the difference (in the present paper $P - P_e = 12.7$ c.c.) is due to the atom polarisability of a molecule of zero moment. Coop and Sutton¹⁸ have shown that molecules which possess several polar groups, whose moments may be opposed and cancel out in the undistorted molecule, may possess a high atom polarisability due to the moments induced by the bending of the groups relative to one another. For example, stannic chloride, bromide and iodide, measured in the vapour state, show $P - P_e = 10.3$ c.c., 8.8 c.c. and 14.5 c.c. respectively. The aluminium bromide molecule (Al_2Br_6) may therefore be taken to have zero moment also in cyclohexane solution.

The molecular weights are calculated from the freezing-point depressions, on the assumption of a cryoscopic constant of 200° (per 100 g. solvent) for cyclohexane (Mascarelli and Benati¹⁹).

In the calculation of the molar polarisability in cyclohexane-ethyl bromide solutions, in order to compare with bromobenzene, the partial molar polarisabilities of the ethyl bromide and cyclohexane have been subtracted from the total polarisability and the difference divided between the supposed AlBr_3 molecules, the complexity being unknown. This, of course, is an arbitrary procedure, but gives an approximate lower limit to the polarisability of the complex compound, which, according to its concentration, may have a polarisability many times this value. The fact that this figure is so high is sufficiently striking. The same procedure with the cyclohexane-bromobenzene solutions gives an apparent polarisability for the aluminium bromide which is little different from that in cyclohexane alone.

¹³ Fairbrother, *Proc. Roy. Soc. A.*, 1933, **142**, 173.

¹⁴ Hartshorn and Oliver, *ibid.*, 1929, **123**, 664.

¹⁵ Nespital, *Z. physik. Chem. B*, 1932, **16**, 153.

¹⁶ Plotnikow, Scheka and Jankelewitsch, *Mem. Inst. Chem. Acad. Ukrain. S.S.R.* 1938, **4**, 382.

¹⁷ Nespital, *Z. Elektrochem.*, 1931, **37**, 559.

¹⁸ Coop and Sutton, *J. Chem. Soc.*, 1938, 1269.

¹⁹ Mascarelli and Benati, *Gazz. Chim.*, 1909, **39**, 642.

TABLE I.—ALUMINIUM BROMIDE IN CYCLOHEXANE.

f_2 .	ϵ .	d .	P_2 (c.c.).	P_0 (c.c.).	f.p. dep. °	Mol. wt.
0	2.0150	0.7736	—	—	—	—
0.006595	2.0225	0.7858	44.4	32.9	—	—
0.01366	2.0293	0.7970	47.4	34.5	1.65	533
0.02042	2.0358	0.8109	43.9	30.3	2.45	540
0.02378	2.0406	0.8176	46.0	32.1	2.97	520
0.04310	2.0606	0.8507	45.2	—	—	—
			Av. 45.4	32.5		Av. 531 (Theor. Al_2Br_6 533)

ALUMINIUM BROMIDE—BROMOBENZENE IN CYCLOHEXANE.

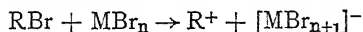
f_2 (AlBr_3).	f_3 (RBr).	ϵ .	d .	ΣP (c.c.).	P_2 (c.c.).	P_3 (c.c.).
0	0.04981	2.1565	0.8075	30.23	82.63	—
0.02254	0.04869	2.1816	0.8470	30.61	(82.63)	47.3
0.04777	0.04629	2.2043	0.8909	30.93	(82.63)	46.2

ALUMINIUM BROMIDE—ETHYL BROMIDE IN CYCLOHEXANE.

f_2 (AlBr_3).	f_3 (RBr).	ϵ .	d .	ΣP (c.c.).	P_2 (c.c.).	P_3 (c.c.).
0	0.07457	2.3032	0.8076	32.23	91.14	—
0.02446	0.07274	2.6152	0.8505	39.87	(91.14)	345
0.01126	0.07373	2.4802	0.8277	36.32	(91.14)	395

It is possible that there may be some formation of a dipole pair $\text{Br}_3\text{Al} \cdot \text{BrC}_2\text{H}_5$ in which the moments would be additive, but this $\leftarrow + \quad \leftarrow +$ cannot be the major factor in the great increase of polarisability observed, as the dipole of bromobenzene, which is more than 80 % of that of ethyl bromide, shows no such effect. It is very probable that the increase of polarisability is caused by a relatively small proportion of ion pairs with high dipole moments. It may be noted that some of the tetra-alkyl ammonium salts, which are soluble in benzene, have dipole moments of 8-20 D. and molar polarisabilities of 1500 to 1800 c.c. Kraus²⁰).

A review of the energies involved in the change



(Fairbrother¹⁰), suggests that even in the case of aluminium bromide in solution with the less easily ionisable alkyl halides, the over-all process is endothermic, with a relatively small equilibrium concentration of ion pairs. There is marked elimination of HBr from solutions of aluminium bromide and the tertiary butyl halides, which are more easily ionisable, presumably arising from a higher concentration of carbonium ion. There are many inorganic halides which function as Friedel-Crafts catalysts and exchange their halogen atoms with those of organic halides, but which form complex anions with much less liberation of energy than

²⁰ Kraus, *Science*, 1939, 90, 281.

does aluminium bromide. In these cases it is to be expected that the concentration of ion pairs will be still less.

These results suggest that the aluminium halides would not easily form stable crystalline compounds of the type $\text{Br}_3\text{Al} \cdot \text{BrR}$, with organic halides, except in those cases in which the separation of the ionic state of the valence bond $\text{R}^+ \text{Hal}^-$ lies only a small distance above the covalent state $\text{R} \cdot \text{Hal}$, *i.e.* in those cases in which the ionisation potential of the radical R is relatively low. A large number, however, of stable compounds between aluminium halides and organic compounds have been prepared by several authors, but in the list given by Gmelin,²¹ of 93 binary compounds with aluminium chloride and 67 with aluminium bromide, only two are compounds between the aluminium salt and a halide containing no nitrogen or oxygen, namely triphenyl-methyl chloride and 3 Brom 1.2.3. triphenyl indene. It is a matter for conjecture, therefore, as to whether the formation of many of these double compounds has any *direct* bearing on the mechanism of the Friedel-Crafts reactions discussed here, except to slow down the reaction when less than molar quantities of catalyst are used, by lowering the equilibrium concentration of the latter in the system. In this connection it may be recalled¹⁰ that the dissolution of aluminium bromide in nitrobenzene in the proportion of about 1 mol. in 2½ mols., effects a very large reduction in the rate of exchange of radio-bromine with ethyl bromide. The presence of nitrogen and/or oxygen in almost all these stable double compounds suggests that stable bonds may be formed between these elements and the aluminium, rather than with the halogen atom.

The foregoing deals only with the relationships between the inorganic catalyst and the organic halide. There remain still to be discussed the questions of the relation between the catalyst and the other partner to the reaction, as well as the final stage in which both organic compounds, in some form, participate. These must form the subject of separate investigations.

One observation in this connection may be noted, however. Repeated attempts to obtain an exchange of bromine between stannic bromide and allyl bromide, resulted always in only a very small exchange. This was surprising in view of the general reactivity of allyl bromide. It was subsequently found, however, that the addition of an olefine—cyclohexene—greatly reduced the rate of exchange between stannic bromide and tert-butyl bromide. Since the allyl bromide, in the former experiments, was always greatly in excess of the stannic bromide, it must be concluded that a complex compound is formed between the ethylenic bond and the stannic bromide, which hinders the catalytic activity of the latter.

The relationship between ethylenic and aromatic bonds, and inorganic halide catalysts is of primary significance over the whole range of Friedel-Crafts reactions. The measurement of the dielectric polarisability offers a method of demonstrating the existence of other polar complexes which have been postulated to account for observed reactions.

Summary.

A primary stage in the Friedel-Crafts reactions of alkylation and acylation is the transition of the covalent carbon-halogen bond into an essentially

²¹ Gmelin, *Handb. anorg. Chem. A1* (8), 1933, pp. 213, 232.

ionic bond, through complex formation with the metal halide catalyst. Evidence for this is given by the radio-isotopic exchange of halogen atoms between the organic and inorganic halides. Additional evidence for the formation of a complex of high dipole moment, probably an ion pair, between aluminium bromide and ethyl bromide is given by the dielectric polarisability which shows a large increase when aluminium bromide and ethyl bromide are dissolved together in cyclohexane. In contrast, bromobenzene and aluminium bromide show no increase, the polarisability of the ternary mixture being very nearly the sum of the partial polarisabilities of its components.

I am indebted to Messrs. Imperial Chemical Industries Ltd., for a grant for the purchase of apparatus.

*Chemistry Department,
The University,
Manchester.*

GENERAL DISCUSSION

Prof. C. K. Ingold (*London-Aberystwyth*) said: Fairbrother's evidence, together with that of Wertyporoch, makes it almost certain that the alkyl group enters into the Friedel-Crafts reaction as the active cation of the complex $R^+(AlCl_4)^-$. However, this conclusion leaves untouched the question of whether the aromatic hydrocarbon reacts as such, or whether it also undergoes some essential preliminary change through the agency of the aluminium halide. The dealkylation of alkyl benzenes, and the alkyl-transfer reactions (*e.g.*, toluene \rightarrow benzene + xylenes), are usually considered¹ to be dependent on a retrograde Friedel-Crafts reaction; but this view implies that a hydrogen halide is involved, a point which, as far as I know, has not been experimentally established. Furthermore, the retrograde Friedel-Crafts reaction would presumably involve the active-proton complex $H^+(AlCl_4)^-$ as reagent; and although this would certainly effect hydrogen exchange,² just as all very strong acids do,³ *e.g.*, $H^+(HSO_4)^-$, it would not be expected to displace alkyl groups. Aromatic hydrocarbons and aluminium halides are known to form complexes, and the dealkylation and alkyl transfer reactions are generally considered to prove that deep-seated chemical effects can follow this interaction.¹ It is possible, however, that these facts should be dissociated, much more than they have been, from the body of evidence from which the mechanism of the Friedel-Crafts reaction itself must be deduced. Fairbrother's observations on the inhibitory effect of olefins on his halogen exchanges is perhaps to be taken as a hint that the molecular conditions for dealkylation, far from being essential also to the Friedel-Crafts reaction, are really part of another story, and are, if anything, inhibitory to the Friedel-Crafts reaction proper. I am suggesting that in the latter process the aromatic hydrocarbon may after all react without essential preliminary change: at least this simplifying possibility should not be overlooked. If it is true, Fairbrother's investigations have already elucidated the nature of the Friedel-Crafts reaction much more completely than seems to be envisaged in his relegation of the behaviour of the aromatic hydrocarbon to future researches.

Dr. Fairbrother, in reply (*communicated*): It is quite possible, as Ingold suggests, that the carbonium-aluminium halide complex ion-pair may

¹ Nightingale, *Chem. Rev.*, 1939, **25**, 347; and *op. cit.*

² Klit and Langseth, *Z. physikal. Chem.*, A, 1936, **176**, 65.

³ Ingold, Raisin and Wilson, *Nature*, 1934, **134**, 734; *J. Chem. Soc.*, 1936, 915; *ibid.*, p. 1637.

react with the hydrocarbon without a preliminary change in the latter in the presence of the catalyst. This is still an open question. On the one hand, aromatic and ethylenic hydrocarbons form complexes with aluminium halides and benzene will react with unsaturated hydrocarbons in the presence of aluminium chloride.⁴ On the other hand, the organic halide-aluminium halide complex is certainly much more reactive than either of its components, even towards a saturated hydrocarbon: for example, separate solutions of aluminium bromide in cyclohexane and ethyl bromide are stable at room temperature but slowly evolve HBr when mixed.

⁴ Milligan and Reid, *J. Amer. Chem. Soc.*, 1922, 44, 206; Berry and Reid, *ibid.*, 1927, 49, 3142.

THE MECHANISM AND KINETICS OF REACTIONS INVOLVING FREE RADICALS.

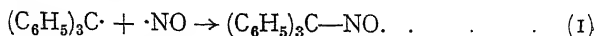
BY W. A. WATERS.

Received 15th August, 1941.

1. General.

Controversy regarding non-ionic processes in solution has chiefly been directed to deciding (a) whether *neutral* radicals can be formed by molecular decomposition and (b) whether these radicals have a sufficiently independent existence to be truly termed *free*. Both these questions have been adequately reviewed quite recently,^{1, 2} and though one must admit that when radicals of short life are concerned it is not possible to obtain indubitable physical evidence, by magnetic measurements, of their neutral character; it is evident that conclusions reached by pointing out analogies are supported by a very large number of concordant experimental facts.

The underlying theoretical conceptions depend upon evidence obtained from the study of gas reactions, and it has been concluded that free radical reactions are, in general, chain reactions which follow more complicated kinetic laws than do ionic interchanges. In the gas phase free radicals do not combine directly, but need the presence of a third particle to take up the liberated energy, whilst, in contrast, substitution is easy and usually requires very little activation energy. In the liquid phase the direct combination of radicals *can* occur, since contiguous molecules are always available, but again substitution reactions are so facile that the radicals of high intrinsic energy interact almost immediately with vicinal solvent molecules. The recombination of two free radicals in solution becomes more and more the prevalent reaction as the intrinsic energy of the radical decreases and the activation energy for its interaction with a stable solvent molecule increases. Thus one finds that the very reactive radical, phenyl, $C_6H_5\cdot$, reacts with solvents such as benzene, carbon tetrachloride and carbon disulphide, whilst triphenylmethyl, $(C_6H_5)_3C\cdot$ which is stabilised by resonance, does not react with most solvents, but will combine at once with another free radical, *e.g.*,

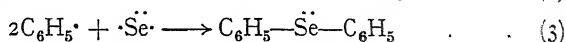
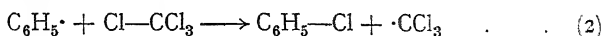


¹ Hey and Waters, *Chemical Reviews*, 1937, 21, 169.

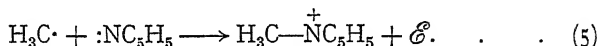
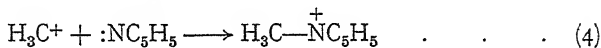
² Hey, *Chemical Society, Annual Reports*, 1940, 37, 250-290.

2. Electrophilic Character of Neutral Radicals.

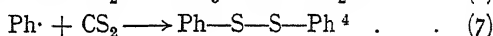
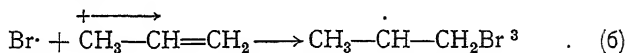
When a covalent molecule dissociates into ions the two fragments have *different* chemical characteristics. Thus when $A-B$ gives A^+ and B^- , A^+ is kationoid (electrophilic) and B^- is anionoid (nucleophilic), but when $A-B$ gives $A\cdot$ and $B\cdot$ both fragments have the *same* chemical character, though not necessarily to the same degree. Apart from the free metals, such as sodium vapour, which tend to lose an electron, the free radicals have depleted electron shells, and in all their reactions tend to share an extra electron: *e.g.*,



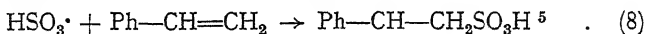
Hence one must classify free radicals as electrophilic reagents although they do not, like organic cations, tend to combine with the unshared electron pairs of such stable molecules as water or pyridine. For a cation this reaction (4) is simple, but for a free radical the corresponding change (5) is a substitution process involving the extrusion of an electron.



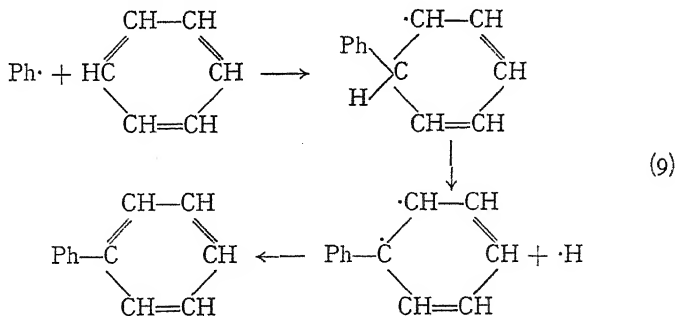
The electrophilic character of free radicals is most clearly shown by their addition reactions with olefines, since preferential attack occurs at points of high electron density: thus:—



(contrast the reaction of $PhMgBr$ with CS_2)



One must classify the phenylation of aromatic rings by free radicals as an addition process, which proceeds as follows:—



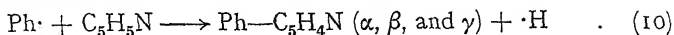
* In this paper a fine point is used throughout to denote a single electron: a covalent bond is indicated by a line.

³ Kharasch and Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2468; Kharasch, Engelmann and Mayo, *J. Organic Chem.*, 1937, **2**, 288.

⁴ Waters, *J. Chem. Soc.*, 1937, 113, 2014.

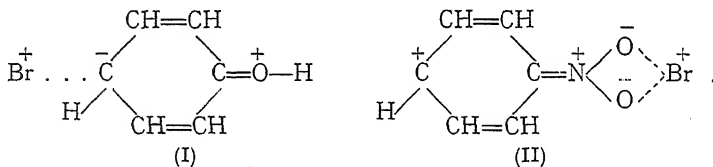
⁵ Kharasch, May and Mayo, *J. Organic Chem.*, 1938, **3**, 175; Kharasch, Schenck and Mayo, *J. Amer. Chem. Soc.*, 1939, **61**, 3092.

These aromatic substitution reactions, and also the characteristic reaction with pyridine,^{6, 7}



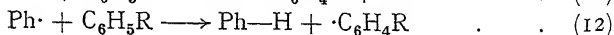
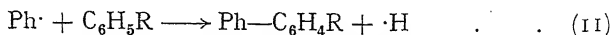
however, make it evident that one must not push too far the analogy between the reactions of neutral radicals and those of active cations. The marked feature of the aromatic substitution reactions of neutral radicals is the fact that they do *not* follow the normal "laws of aromatic substitution" which are applicable both for cations and for reagents, such as nitric acid, which give kationic groups during the course of their attack on the aromatic ring. Neutral radicals give all three isomerides (the *para* often predominating) in their attack on any aromatic compound, $\text{C}_6\text{H}_5\text{R}$, and it is evident therefore that the normal "polarity effects" of the substituent group, R, are not called into operation.

One can easily see the reason for this. When an active ion approaches an aromatic molecule, or indeed any structure in which there is resonance, its electrical field perturbs the structure of the molecule attacked. The mesomeric state is then converted, by a tautomeric ($\text{T} \rightleftharpoons$) change into another structure with which the active ion may (or may not) be able to combine. Thus when Br^+ approaches phenol there is formed (I), and *para* (or similarly *ortho*) substitution can easily result, whilst with nitrobenzene (II) is formed, and is not prone to nuclear kationoid attack.



Neutral atoms, such as free bromine, $\text{Br}\cdot$, or radicals such as phenyl, $\text{Ph}\cdot$, can, however, approach to the immediate vicinity of a resonance system without appreciably perturbing its normal structure. Only the electrostatic "Field" effect of the substituent group, R, not even including its "Inductomeric effect"⁸ remains to affect the relative electron density at the aromatic carbon centres. These electrostatic forces vary in magnitude with distance and vector orientation but do not lead to any alternation in polarity around an aromatic ring.

Moreover, the attack of a free phenyl radical on any nuclear carbon atom of an aromatic compound requires very little activation energy, and hence it is the vicinity of a particular carbon atom to the free radical rather than its local electron density which determines whether reaction will take place. Confirmatory evidence that proximity factors are more significant than activation energy factors in these free radical substitutions may be adduced from the fact that the reactions (11 and 12) both occur together.^{2, 7}



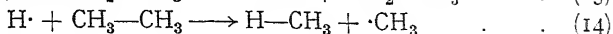
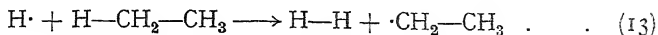
⁶ Haworth, Heilbron and Hey, *J. Chem. Soc.*, 1940, 349, 358, 372; Butterworth, Heilbron and Hey, *ibid.*, 355.

⁷ Heilbron, Hey and Lambert, *ibid.*, 1279.

⁸ Ingold, *Chemical Reviews*, 1934, 15, 233.

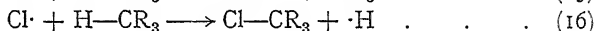
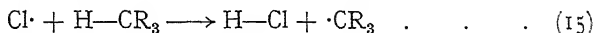
3. Mechanism of Attack on Single Bonds.

The mechanism of the attack of free atoms of hydrogen on the vapours of paraffin hydrocarbons is still a matter of controversy.⁹ Thus the initial reaction with ethane may be either (13) or (14).



On the whole, the experimental evidence seems to favour mechanism (14) which accords with the view that it is the weaker covalent bond which breaks the more readily.

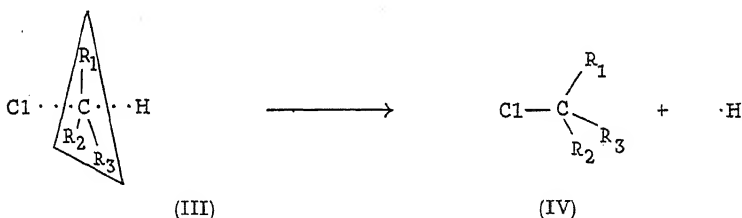
Atomic chlorination should be exactly similar, and both reactions (15) and (16) are possible initial stages of the substitution process.



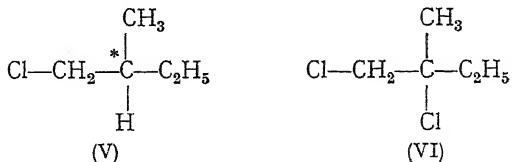
Brown, Kharasch and Chao¹⁰ have pointed out that attack on an optically active paraffin, $\text{H}-\text{CR}_1\text{R}_2\text{R}_3$ by a chlorine atom by mechanism (15) should yield a free hydrocarbon radical, $\cdot\text{CR}_1\text{R}_2\text{R}_3$ with a planar configuration¹¹ and consequently the subsequent reaction, (17),



should give an optically inactive racemic product, whilst, on the other hand, reaction by mechanism (16) should proceed *via* the complex (III), through a Walden inversion, to give an optically active product (IV).



They chlorinated active amyl chloride (V) to 1:2-dichloro-2-methylbutane (VI), both photochemically, and by the use of sulphuryl chloride and benzoyl peroxide¹² and, in each case, found that their product was *not* optically active.



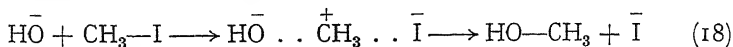
⁹ Steacie and Parlee, *Trans. Faraday Soc.*, 1939, **35**, 854; Trenner, Morikawa and Taylor, *J. Chemical Physics*, 1937, **5**, 203; Steacie, *Chemical Reviews*, 1938, **22**, 311.

¹⁰ Kharasch, Brown and Chao, *J. Amer. Chem. Soc.*, 1940, **62**, 3435.

¹¹ Compare Wallis and Adams, *ibid.*, 1933, **55**, 3838.

¹² Kharasch and Brown, *ibid.*, 1939, **61**, 2142.

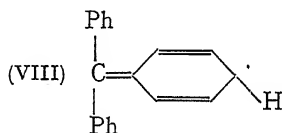
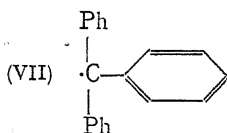
This is conclusive evidence for the rejection of chlorination mechanism (16) which, as will be seen, postulates the existence of a transition complex (III) in which the central carbon atom holds *nine* electrons, without the help of any electrostatic forces equivalent to those which play an essential part in bimolecular ionic changes such as (18).



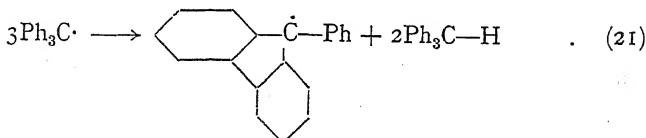
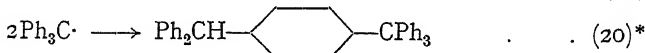
The assertion that whenever a free radical attacks a saturated molecule it reacts only with one of the peripheral atoms is in full accord with all the experimental evidence that one can adduce from the study of their reactions in solutions, and it would seem therefore that the experimental evidence concerning the mechanism of the gas reactions mentioned above should be subjected to a critical review.

4. Mesomeric Free Radicals.

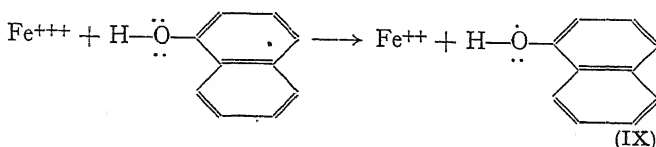
It is now agreed that in free radicals such as triphenylmethyl the domain of the odd electron is distributed throughout the whole of the conjugated system, so that structures such as (VII) and (VIII) participate in the resonance system.



Radicals which are resonance systems would therefore be expected to react with other molecules, or to unite with themselves, to give more than one type of product, and the following reactions of triphenylmethyl illustrate that this is true.

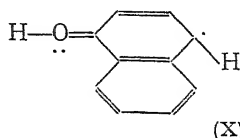


A similar mesomerism is possible in the semiquinonoid radicals which result from the oxidation of phenols and amines by reagents such as ferric chloride, potassium ferricyanide, or persulphates—compounds which abstract only *one* electron: thus—



* Reaction (20), which is catalysed by acids, may be ionic, and due to attack on Ph_2CH by Ph_3C^+ , but the photochemical reaction (21) cannot easily be interpreted in this alternative way.

mesomeric with (X)



Substances of this type have a measurable stability,¹³ undoubtedly due to internal resonance, and dimerise instead of reacting immediately with the surrounding solvent molecules. Sir R. Robinson¹⁴ has recently discussed the courses of the intramolecular electron changes which can take place in oxidative reactions of this type, amongst which must be included many enzyme reactions of great biochemical interest.

5. Kinetic Characteristics of Free Radical Reactions.

The velocities of all chemical reactions due to free radicals are primarily dependent upon the rates of production of the radicals from more stable covalent molecules. This has been verified for reactions of relatively stable free radicals, such as triphenylmethyl, with iodine,¹⁵ nitric oxide,¹⁶ and oxygen,^{17, 18} for short-lived radicals such as phenyl, which react with vicinal solvent molecules,¹⁹ and for many photochemically-activated chain reactions.

Of the reactions of triphenylmethyl and its analogues little more need be said than that it is evident that the activation energy for the recombination of stabilised radicals in solution, though not zero, is very small indeed²⁰ and that appreciably more energy is needed for reaction with a covalent molecule. Attention may be directed, however, to the ease with which chain reactions, which ultimately involve stable molecules, may be set up.²¹

The fact that reactions such as (2), (11) and (12), involving phenyl radicals, apparently proceed, in dilute solution, at approximately equal rates (actually that of eqn. 22) in all solvents indicates that the activation energy for these bimolecular reactions with solvent molecules is fairly small (of the order of 1 to 5 k.cal.) for otherwise the phenyl radicals would have a sufficient free life to intermingle and recombine, in the same way as do radicals of triphenylmethyl. However, even if the probability of reaction between a phenyl radical and a solvent molecule were one in several hundred the chance of mutual collision of two free phenyl radicals would be very small, since, as Franck and Rabinowitch have pointed out,²² each radical is much more likely to undergo an energy-transferring collision with one of the solvent molecules which are continually in its proximity than with other solute molecules. The reservation that the mass-action laws can only be applied to *relatively slow* reactions in the liquid phase has an important bearing on the

¹³ Michaelis *et al.*, *Chemical Reviews*, 1935, **16**, 242; 1938, **22**, 437; *J. Amer. Chem. Soc.*, 1938, **60**, 202, 1678.

¹⁴ *J. Chem. Soc.*, 1941, 232.

¹⁵ Ziegler, Ewald and Orth, *Annalen*, 1930, **479**, 277.

¹⁶ Ziegler, Orth and Weber, *ibid.*, 1933, **504**, 151.

¹⁷ Ziegler, Ewald and Seib, *ibid.*, 182.

¹⁸ Conant and Evans, *J. Amer. Chem. Soc.*, 1929, **51**, 1920.

¹⁹ Grieve and Hey, *J. Chem. Soc.*, 1934, 1800.

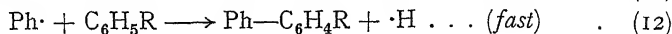
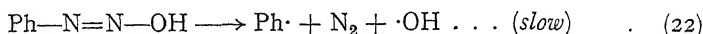
²⁰ Ziegler, *Trans. Faraday Soc.*, 1934, **30**, 13.

²¹ Ziegler and Ewald, *Annalen*, 1933, **504**, 162.

²² Franck and Rabinowitch, *Trans. Faraday Soc.*, 1934, **30**, 120.

kinetics of all free radical reactions, including those which are catalysed chain processes (see below).

As a substitution process, such as the Gomberg reaction,

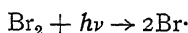
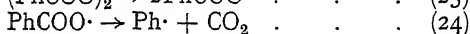
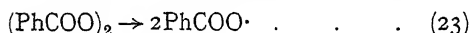


proceeds, the composition of the solvent, originally $\text{C}_6\text{H}_5\text{R}$, will gradually alter, both through the formation of the desired reaction product, and through undesired reactions, analogous to (12) due to the concomitantly produced radicals $\cdot\text{H}$, $\cdot\text{OH}$, etc. Hence, although the initial order, and rate, of reaction is that given by equation (22) quantitative yields are not obtained, and undesirable by-products (frequently polymeric tars) are formed. Much cleaner reaction products can be obtained by adding other reagents, *e.g.*, metals, which combine with the unessential free radicals.²³

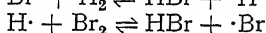
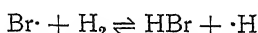
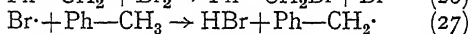
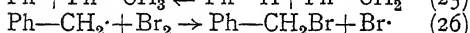
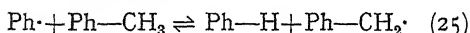
6. Kinetics of Catalysed free Radical Reactions.

Very few catalysed free radical reactions in solution have been investigated kinetically, though experimental work in this field would be of great interest. The following scheme serves to show that reactions initiated by substances such as benzoyl peroxide should resemble very closely photochemical gas reactions, which have received much detailed study.

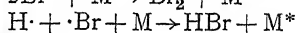
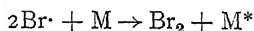
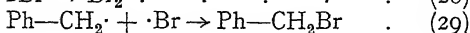
Stage 1. Radical formation (*slow*).



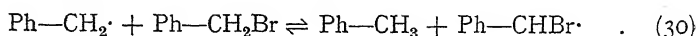
Stage 2. Chain sequence (*all reactions faster than 1*).



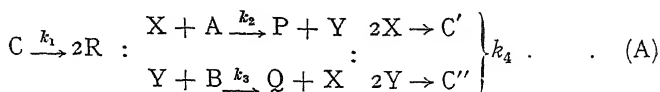
Stage 3. Chain breaking (*all reactions very fast in solutions*).



Side reactions (*which do not break chain, but which reduce the overall rate of formation of reaction product*).



All the essential features of these catalysed substitution reactions can be represented schematically as follows:—



²³ Compare Waters, *J. Chem. Soc.*, 1937, 1113; 1939, 864.

where C is the catalyst which dissociates into radicals R,

X and Y are the radicals in the chain reaction,

A and B are the main reactants, and P and Q the main reaction products,

C' and C'' are the final stable products formed from the catalyst, or from the intervening radicals X and Y.

The whole reaction may be divided into two phases:—

Phase I.—Very rapidly terminated, and probably not measurable kinetically—free radicals are formed from the catalyst. After time t there are $2C(1 - e^{-\frac{1}{2}k_1 t}) = (\text{approx.}) k_1[C]t$ reaction chains in progress. During this initial phase of reaction, the rate of formation of the main products, $dP/dt = k \int_0^t [R]dt$ increases rapidly. If k_1 is large, this initial acceleration of the reaction leads to an uncontrollable temperature change, and possibly to explosion conditions.

Phase II.—Very quickly, in most cases, there will be reached a balance between the rate of formation of new radicals and their rate of destruction by recombination in pairs.

Then we have

$$dR/dt = k_1[C - R/2] - k_2[R]^2 = 0 \quad . \quad . \quad (B)$$

and since, as mentioned in Section 5 above, $k_2 \gg k_1$, a state of relative equilibrium is reached at which

$$[R] \doteq K[C]^{\frac{1}{2}} \cdot e^{-\frac{1}{2}k_1 t}; \text{ where } K = (k_1/k_2)^{\frac{1}{2}} \quad . \quad . \quad (C)$$

This state of relative balance as to the total number of radicals present, and therefore of the total number of reaction-chains, holds throughout the main course of the substitution process, for which one can derive a theoretical reaction rate as follows:—

We have

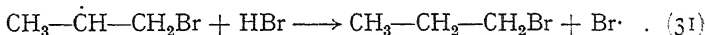
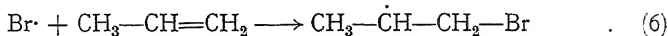
$$[X] + [Y] = [R]$$

$$\text{and} \quad dX/dt = dY/dt = k_2[X][A] - k_3[Y][B] = 0,$$

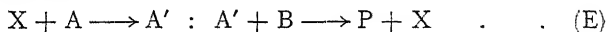
consequently

$$\begin{aligned} d[P]/dt &= d[Q]/dt = k_2[X] \cdot [A] = k_3[Y] \cdot [B] \\ &= \frac{k_2 k_3 [A] \cdot [B] \cdot [R]}{k_2 [A] + k_3 [B]} = \frac{k_2 k_3 [A] \cdot [B] [C]^{\frac{1}{2}} \cdot K \cdot e^{-\frac{1}{2}k_1 t}}{k_2 [A] + k_3 [B]} \quad . \quad (D) \end{aligned}$$

For a chain addition reaction, *e.g.*,



which may be represented as



the same kinetic equation can be derived.

The reaction velocity decreases with time, and is dependent upon the exponential rate at which the catalyst is used up. Side reactions between any of the active radicals and any of the reaction products will produce a further exponential decrement in the overall rate of reaction by diminishing the effective concentration of the active radicals.

This will occur even when the side reaction is reversible (*e.g.*, 30) and does not lead to the formation of other reaction products (compare Section 7b).

7. Solvent Effects.

(a) One Reactant is the Solvent.

Equation (D) of the previous section can also be written

$$\frac{d[P]}{dt} = -\frac{d[A]}{dt} = \frac{k_2[A]}{\left(1 + \frac{k_2[A]}{k_3[B]}\right)} \cdot K[C]^{\frac{1}{2}}e^{-\frac{1}{2}k_1t} \quad (F)$$

and thus when any one reactant (B) is present in *large* excess the reaction velocity is proportional to the concentration of the other (A). Moreover, the reaction velocity $d[P]/dt$ should be increased by increasing the dilution of A in B. In this connection it is interesting to note that Kharasch, White and Mayo²⁴ have already commented on the fact that when bromine reacts, in solution in toluene, to give benzyl bromide the reaction velocity is increased by increasing the dilution of the bromine.

Many polymerisations in the liquid phase, *e.g.*, of styrene, are free radical addition reactions, for which $A = B$, that proceed with velocities given approximately by equation (F).²⁵ In the presence of an inert diluent the reaction velocity is proportional to the concentration of the monomer, and, after an initial rapid rise (Phase I above), falls exponentially with the decay of the catalyst. When the monomer is itself the solvent the reaction velocity should, of course, become of zero order with respect to it until the polymerisation has been very largely completed. Norrish and Brookman²⁶ have shown that the polymerisations of styrene and of methyl methacrylate, when catalysed by benzoyl peroxide, follow this course, and that the reaction velocity remains of zero order for some considerable time. This state of affairs can be reached only when the rate of formation of free radicals, k_1 , is very much smaller than the rate of *all* the subsequent reactions, so that the principal reaction is complete long before all the catalyst is used up.

This is not the general rule with catalysed free radical reactions, for frequently the reaction ceases before quantitative yields of the main reaction products have been obtained. When this is the case it is advisable to add the catalyst gradually during the course of the reaction and not in one initial portion.²⁴ Side reactions can, of course, be minimised by using a large excess of one of the main reactants.

(b) The Solvent is a Diluent.

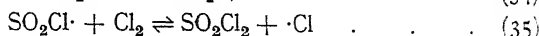
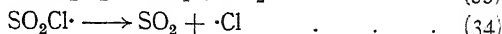
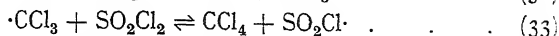
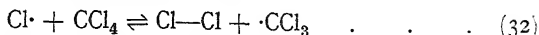
In section 1 it was pointed out that active free radicals, such as phenyl, or atomic chlorine, reacted with nearly all solvents, whereas the less active free radicals, such as triphenylmethyl or atomic iodine, reacted almost exclusively with other radicals. Nevertheless it is not true to say that the highly active free radicals are always destroyed by solvents, since, though substitution will rapidly lead to a change in the

²⁴ Kharasch, White and Mayo, *J. Organic Chem.*, 1938, **3**, 35.

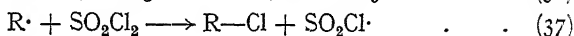
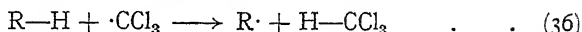
²⁵ Schulz and Husemann, *Z. physikal. Chem.*, B, 1936, **34**, 187; 1937, **36**, 184; 1938, **39**, 246.

²⁶ Norrish and Brookman, *Proc. Roy. Soc., A*, 1939, **171**, 147.

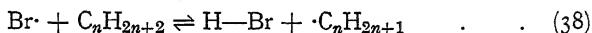
identity of the active particles, their chemical type can often persist for a very long time. For instance, intensely reactive atomic chlorine, generated from sulphuryl chloride by benzoyl peroxide catalysis,¹² is an effective chlorinating agent even in dilute solution in carbon tetrachloride. In this solvent the apparent life of atomic chlorine is due to its regeneration by the reactions (32) to (35).



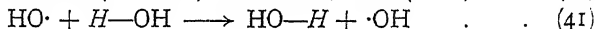
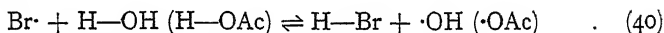
It would be interesting to test the carbon tetrachloride, at the end of the chlorination reaction, for the presence of a trace of chloroform, for the side reactions (36) and (37) might well occur.



Similarly the peroxide-catalysed addition of hydrogen bromide to olefines (eqns. 6 and 31) can be carried out, though at greatly varying rates, in a large number of solvents, such as ligroin, acetic acid, and water, which undoubtedly react both with neutral alkyl radicals and with atomic bromine.^{3, 27} In this process still more complicated sets of side reactions are possible. Thus in hydrocarbon solvents reactions (38) and (39) can occur,



whilst in water or organic acids there can also occur reactions such as (40) and (41).



Reaction (39), which leads to the formation of a polymeric hydrocarbon incorporating solvent molecules in its structure, may occur when any olefine is polymerised by free radicals in the presence of a diluent.

The forward reaction (40) leads to the replacement of an active radical (*e.g.*, atomic bromine) by a very much less active one (*e.g.*, hydroxyl), and, since the reverse change may require a considerable amount of activation energy, the concentration of the active radical, and consequently the overall rate of the addition reaction (eqn. 6), is very greatly reduced. Nevertheless, the overall rate of destruction of radicals may not be greatly affected, since, though the radicals formed from the solvent will rapidly lose their identities, on account of exchanges such as (41), they will not change their species. It is on account of the occurrence of the exchange (41) that slow oxidations by peroxides in aqueous solution may still be due to the presence of neutral hydroxyl radicals,²⁸ and oxidations by lead tetra-acetate in glacial acetic acid solution due to neutral acetate radicals.²⁹

²⁷ Kharasch and Potts, *J. Amer. Chem. Soc.*, 1936, **56**, 57.

²⁸ Compare Haber and Weiss, *Proc. Roy. Soc., A*, 1934, **147**, 333.

²⁹ Compare Waters, *J. Chem. Soc.*, 1939, 1806; Criegee, Kraft and Rank, *Annalen*, 1933, **507**, 159.

8. Inhibitors of Free Radical Reactions.

Retarding reactions, such as (40), by which an active free radical is converted into a much less reactive one, may, in many solvents, reduce the concentrations of the active radicals (X and Y of Section 6) to such an extent that the main chain propagation processes are much less rapid than the chain-termination processes (*i.e.* $k_4 \gg k_2$ and k_3). When this is the case the solvent would be regarded as an inhibitor of a free radical reaction in which there was no means of regeneration of the active catalyst; the same solvent might not be an effective inhibitor of a reaction in which the dissociation of some molecules into neutral radicals was continually occurring (*e.g.*, a photo-bromination).

True inhibition of free radical reactions is brought about only by chain-breaking due to (*a*) union of two radicals, or (*b*) chemisorption of radicals by surfaces. For all practical purposes, however, solvents can be regarded as inhibitors when, by reaction with active radicals they produce much less active radicals, incapable of attacking the peripheral atoms of most covalent molecules, which by mutual recombination give stable molecules. Thus an inhibitor of a reaction catalysed by benzoyl peroxide must produce a radical $X\cdot$ more stable than the benzoate radical, $\text{PhCOO}\cdot$, which on association to $X-X$ yields a substance less easily dissociated than is molecular benzoyl peroxide.

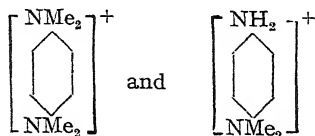
In general, one can say that substances which can give mesomeric radicals (Section 4) satisfy these requirements, and in this connection it must be remembered that molecules which can easily lose an electron are the ideal radical-chain breakers. Hence, though mild reducing agents, such as quinol, thiophenol, nitrosobenzene and iodides, are fairly effective inhibitors of free radical reactions they are surpassed by substances such as triphenylmethyl or nitrogen dioxide.

*The University,
Durham.*

GENERAL DISCUSSION

Dr. J. Weiss (*Newcastle-upon-Tyne*) (*Communicated*): It may be worth pointing out that a close connection exists between free radicals and ions in certain cases. A detailed study will be published in due course but I will now demonstrate this for a few simple cases.

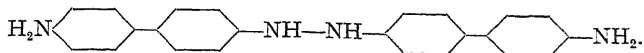
If we treat tetra-methyl-*p*-phenylenediamine, or dimethyl-*p*-phenylenediamine with an oxidising agent in acid solution we get (through a univalent oxidation) monovalent positive ions which are capable of forming salts with various anions. These are the so-called Wurster's salts in which the cations



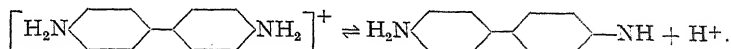
are present.¹ Similarly benzidine on oxidation in acid solutions yields benzidine blue which is also an ionic compound with the monovalent cation $\left[\text{H}_2\text{N} \text{---} \text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_4 \text{---} \text{NH}_2 \right]^+$. The relation to the free radicals is shown

¹ Cf. Michaelis, *Chem. Rev.*, 1935, 16, 243.

here very definitely ² because on decomposition of the benzidine blue we obtain the compound



This is a dimerisation product of the corresponding radical which is formed from the ions through the dissociation equilibrium:



We see here that the connection between the free radical and the ion is given through an acid-base equilibrium. Whenever there is a hydrogen present which can come off as a proton we get the radical which becomes apparent through its dimerisation product.

In general the equilibrium of the reaction: $\text{RH}^+ \rightleftharpoons \text{R} + \text{H}^+$ depends on the proton affinity of the radical and the concentration of the hydrogen ions.

Very often radicals containing nitrogen or oxygen show a considerable proton affinity (weak acids) and the ions will be stable at comparatively low $[\text{H}^+]$ whereas ions with a small proton affinity (e.g. hydrocarbon ions) require a very high $[\text{H}^+]$ for their stabilisation.³ This gives a method of producing the monovalent radicals and their dimerisation products.

As long as the univalent positive ion is stabilised (through a sufficiently high $[\text{H}^+]$) it will not be oxidised further (on account of its positive charge being unfavourable to a further loss of electrons). Under suitable experimental conditions the proton comes off and the dimer is formed.

The significance of the use of concentrated sulphuric acid and an oxidising agent in the formation of certain dimers, e.g., 2-2'-dibenzanthronyl from benzanthrone, the formation of congo red from the corresponding diazo compound) can now be easily understood on the basis of the foregoing considerations.

Dr. W. A. Waters (*Durham*), in reply (*communicated*): The possibility that an ion might possess an odd number of electrons, and so have the chemical characteristics of a free radical was discussed in detail by W. Hückel in 1931.⁴ More recently Michaelis and his colleagues⁵ have produced experimental evidence of the paramagnetism of ions of this type and have shown how their stability varies with the pH of the environment. Dr. Weiss's discussion of the stability of radical cations ($\text{R}^+\text{:H}$)⁺ could be extended to radical anions, of which the metallic ketyls (e.g., $(\text{Ph}_2\text{C}-\text{O}^- \text{K}^+)$) are typical. These are stabilised by alkali. The structural requisites for the stabilisation of radical-ions,—viz., the dispersion of the charge of the odd electron—in no way differ from those for the stabilisation of neutral free radicals.

² Cf. Weiss, *Chem. and Ind.*, 1938, 57, 517.

³ Cf. Weiss, *Nature*, 1941, 147, 512.

⁴ W. Hückel, *Theoretische Grundlagen der Organischen Chemie*, Band I, pp. 120-127 (Leipzig, 1931).

⁵ Michaelis, Schubert, Reber, Kuck and Granick, *J.A.C.S.*, 1938, 60, 1679, and later papers.

MECHANISM OF THE CANNIZZARO REACTION AND SOME ALLIED PROCESSES.

By JOSEPH WEISS.

Received 1st September, 1941.

The conversion of aldehydes into the corresponding alcohol and the acid is of considerable importance in chemistry and biology.¹ In the classical Cannizzaro reaction (C.R.) this conversion takes place under the influence of strong alkali. Consequently, only those aldehydes will give the C.R. which do not undergo aldol condensation under these conditions, *e.g.* formaldehyde, benzaldehyde and those aliphatic aldehydes which have no hydrogen on the α -carbon atom.²

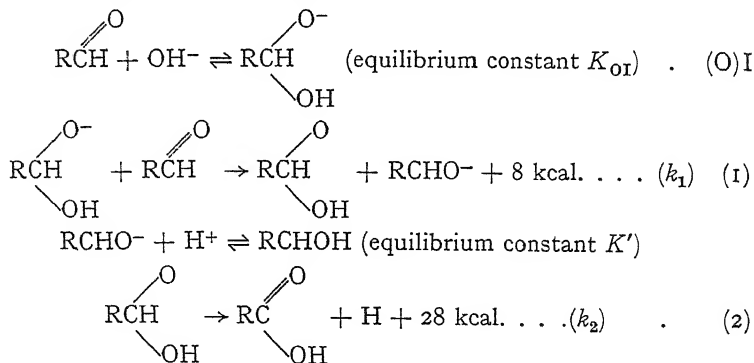
Although much work³ has been done recently on the kinetics of this reaction, its mechanism is still rather obscure. In 1931 Haber and Willstätter⁴ proposed a chain mechanism for the C.R., but this suggestion was more or less disregarded, and was thought to be inconsistent with the known facts. The important point in the Haber-Willstätter theory lies in the introduction of the radicals RCO and RCHOH, both formed from the aldehyde molecule (RCHO) through a (univalent) oxidation or reduction. The actual chain mechanism is of secondary importance, particularly as, in general, the change from a radical chain to a simple radical reaction can be brought about fairly easily.⁵

We now seek to show that much of the experimental evidence can be explained by the Haber-Willstätter theory in a somewhat modified form.

1. The Cannizzaro Reaction.

(a) Mechanism.

The following mechanism is proposed for the Cannizzaro reaction of aldehydes in the presence of alkali in aqueous or dilute alcoholic solutions :



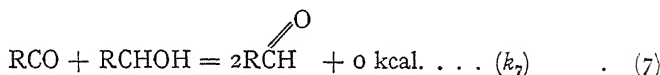
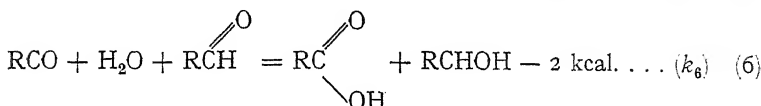
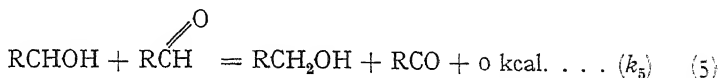
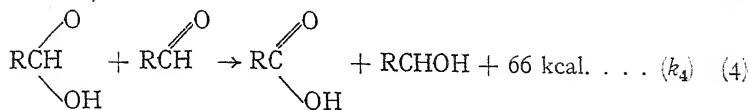
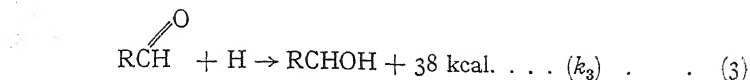
¹ Dixon, *Ergebnisse der Enzymforschung*, 1939, 8, 217.

² Cf. Lieben, *Monatshefte*, 1901, 22, 289.

³ Cf. Lock and Eitel, *Sitzungsber. Akad. Wiss. Wien*, 1939, 148, IIb, 90, 108.

⁴ Haber and Willstätter, *Ber.*, 1931, 64, 2844.

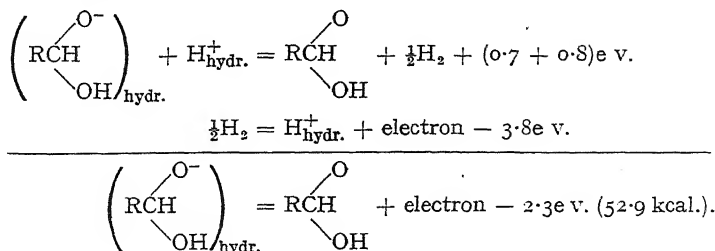
⁵ Haber and Weiss, *Proc. Roy. Soc., A.*, 1934, 147, 332.



Only comparatively simple elementary processes (electron or hydrogen atom transfers) are involved in the above scheme of reactions, for all of which the energy requirements are fulfilled, as will be shown in the following: (The individual bond energies* are taken from Pauling⁶ or Sidgwick⁷).

Equilibrium (0)I.—The formation of the aldehydate ion under the influence of alkali has been assumed by many previous authors,³ and there is also some direct experimental evidence for this reaction.^{7a}

Reaction 1 is a mutual oxidation and reduction between the aldehydate ion and the aldehyde molecule. Aldehydes in alkaline solution show quite definite reducing properties (*e.g.* towards silver salts or oxidising agents) whereas the unchanged aldehyde molecule is of an oxidising character. It is possible to get an estimate of the electron affinity + hydration energy of the aldehydate ion from the potential measurements on aldehydes in alkaline solutions. These give a value (in the case of formaldehyde or acetaldehyde) of about -0.7 v. (25° C., Pt electrode) measured against the hydrogen electrode.^{8, 15} If we correct for the low hydrogen ion concentration ($\sim 10^{-14}$ mol./l.) of the alkaline solution (corresponding to $14 \times 0.058 = 0.81$ v.), we obtain:—



⁶ Pauling, *The Nature of the Chemical Bond* (Ythaca, 1939).

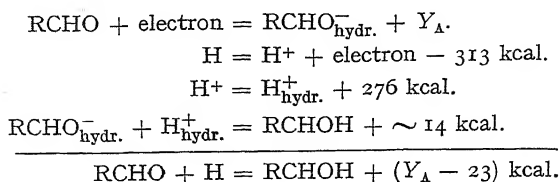
⁷ Sidgwick, *The Covalent Link in Chemistry* (Cornell University Press, 1933).

^{7a} Cf. Herold, *Z physik. Chem., B*, 1932, 18, 266.

* The total energies or (if available) the free energy values have been used. In general the difference does not exceed $\pm 0.5\text{e v.}$ (at ordinary temperatures).

⁸ Rapkine, *J. Chim. Physique*, 1930, 27, 202; Baur, *Ber.*, 1901, 34, 3733.

The electron affinity + hydration energy (Y_A) of the aldehyde molecule can be estimated from the following cycle of reactions :—



With this we have to compare the value obtained for reaction 3 :—

$$38 = (Y_A - 23).$$

This gives the value :—

$$Y_A \sim 61 \text{ kcal.}$$

In reaction (1) we gain the difference of (electron affinity + hydration energy) between aldehyde ion and aldehyde molecule.

Reaction 2.—We gain the difference (115 kcal.) between the single oxygen bond (70 kcal.) and the double oxygen bond in the carboxyl group (182 to 190 kcal.), but we have to break one CH single bond which requires 87 kcal.

Reaction 3.—The (CO) bond strength in aldehydes is about 145 kcal. First we have to open this double bond which requires $\left(\frac{145}{2}\right) = 72.5$ kcal. (or similarly the difference between the double and single C—O bond $145 - 70 = 75$ kcal.) and then we gain the energy of one OH bond (110 kcal.).

Reaction 4.—The total heat of this reaction is obtained by combining reactions 2 and 3.

Reaction 5.—We have to break one CH single bond and gain the energy of another CH single bond, giving, thus, a zero heat of reaction. The value is probably slightly positive, because the CH bond in the aldehydes is not quite so strong as in the alcohols.

Reaction 6.—We gain 38 kcal. through (partial) hydrogenation of the aldehyde (reaction 3), but we have to dissociate the OH bond in water, which requires 110 kcal. and gain the energy of one CO single bond (70 kcal.).

Reaction 7 involves the breaking and formation of one CH single bond.

Meta-hydroxybenzaldehyde gives the ordinary Cannizzaro reaction, whereas the *o*- and *p*-hydroxybenzaldehydes do not react at all under ordinary conditions.⁹ This is due to the mesomeric effect¹⁰ of the OH group, which increases the electron density on the CHO group and inhibits its tendency to be reduced (in reaction 3 and 4), thereby preventing the C.R.

In the C.R. of nitrobenzaldehydes¹¹ no appreciable reduction of the nitro group occurs. This is due to the fact that the CHO group (further activated by the presence of the NO₂ group in the *o*- or *p*-position) is a better acceptor for the hydrogen.

(b) Kinetics.

The kinetics of the Cannizzaro reaction can be derived from the reaction scheme outlined above.

⁹ Lock, *Ber.*, 1929, **62**, 1177.

¹⁰ Ingold, *Chem. Rev.*, 1934, **15**, 225.

¹¹ Lock, *Monatshfte*, 1930, **60**, 855.

In the simplest case the slowest process (reaction 1) is the time determining step, and we obtain :

$$\text{rate} = \frac{d(\text{RCOOH})}{dt} = \frac{d(\text{RCH}_2\text{OH})}{dt} = k_1[\text{RCHO}][\text{RCH}(\text{OH})\text{O}^-] = k_1K_{\text{OI}}[\text{RCHO}]^2[\text{OH}^-]. \quad (8)$$

This corresponds to a third order reaction which is in agreement with the experimental findings of various authors.^{3, 12}

If we subject the above scheme of reaction to a more elaborate treatment and calculate the rate of formation, applying the method of stationary concentrations,

$$\left(\text{i.e. for } \frac{d(\text{RCO})}{dt} = \frac{d(\text{RCHOH})}{dt} = \frac{d(\text{H})}{dt} = \frac{d(\text{RCH}(\text{OH})\text{O})}{dt} = 0 \right)$$

we obtain :—

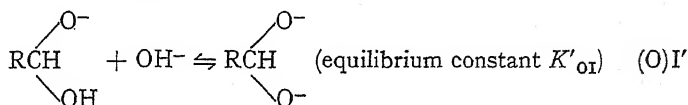
$$\frac{d(\text{RCOOH})}{dt} = k_1K_{\text{OI}}[\text{RCHO}]^2[\text{OH}^-] \left\{ 1 + \frac{\phi}{4} \left(\sqrt{1 + \frac{8k_3k_6}{k_1k_7K_{\text{OI}}[\text{OH}^-]\phi}} - 1 \right) \right\} \quad (8')$$

whereby :

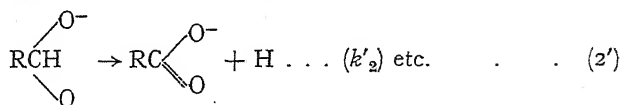
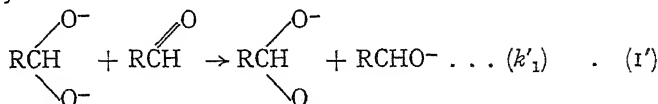
$$\phi = \left(1 + \frac{[\text{H}^+]}{K'} \right).$$

The first term is again of the third order (as above), and the second term (although somewhat different), does not change this result appreciably.

There are possibly two instances¹³ where, under certain conditions, a reaction of approximately fourth order has been observed. This can be accounted for by the above mechanism if we assume that the dialdehyde ion (rather than the aldehyde ion) enters into the reaction.* This is formed according to :—



followed by :



In this case reaction (1') is the time determining step, and one obtains for the rate of reaction :

$$\text{rate} = \frac{d(\text{RCOOH})}{dt} = k'_1K_{\text{OI}}K'_{\text{OI}}[\text{RCHO}]^2[\text{OH}^-]^2 \quad (8'')$$

i.e., a reaction of the fourth order.

¹² Pomeranz, *Monatshefte*, 1900, 21, 389; Molt, *Rec. Trav. chim. Pays-Bas*, 1937, 56, 233; Blanksma and Zaaijer, *ibid.*, 1938, 57, 727; Birstein and Lobanow, *Z. anorg. Chem.*, 1927, 160, 377.

¹³ Geib, *Z. physik. Chem. A.*, 1934, 169, 41; Pomeranz, *loc. cit.*¹²

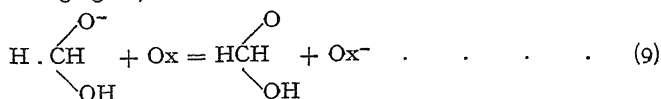
* This depends mainly on the nature of the radical R.

(c) The Radicals.

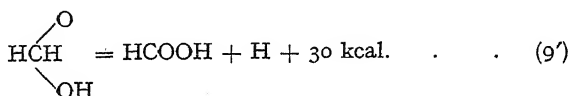
Experimental evidence is also available for the individual reaction steps, and the occurrence of the free radicals assumed in the above mechanism.

Loew¹⁴ observed that on treating formaldehyde with an oxidising agent (Ag_2O , Cu_2O) in alkaline solution, formic acid and molecular hydrogen are formed, the amount of HCOOH being greater than corresponds to the oxygen in the oxide. The same reaction takes place with many other oxidising agents, *e.g.*, CuO ,¹⁵ $\text{K}_3\text{Fe}(\text{CN})_6$,¹⁵ $\text{K}_2\text{S}_2\text{O}_8$,¹⁵ H_2O_2 .¹⁶ It can be represented as follows:—

(Ox = oxidising agent).



followed by:—



Müller¹⁵ then showed that on electrolysing alkaline solutions of formaldehyde, acetaldehyde or benzaldehyde, each farad produces on the anode (Ag or Cu) one equivalent of hydrogen and one molecule of the corresponding acid. This anodic oxidation is also quantitatively represented by the (univalent) oxidation process (reaction 9).

All these experiments show that if an oxidising agent is present in considerable quantity the H atoms primarily formed appear mainly as molecular hydrogen. In the ordinary Cannizzaro reaction the oxidising agent is the aldehyde molecule itself. However, reaction 1 is a slow process, and consequently the H atoms are formed so slowly that they are practically all used in reducing the aldehyde (reactions 3 and 4).

This view is confirmed by the following observations:—

Under suitable conditions oxidising agents actually accelerate the C.R. We have found this to be the case with ferrate, silver oxide and benzoyl peroxide.¹⁷ Moreover, Kharasch¹⁸ and Urushibara and Takebayashi¹⁹ found that the peroxides, formed from the molecular oxygen and the aldehyde, have a considerable accelerating effect, and that under certain conditions the C.R. of benzaldehyde is completely inhibited in the absence of any peroxide. This will be the case if the experimental conditions are such that the normal starting process (reaction 1) does not occur to any appreciable extent. We have also found¹⁷ that $\text{Fe}(\text{OH})_2$ or $\text{Mn}(\text{OH})_2$ inhibit the C.R. of benzaldehyde, probably on account of their reducing action on the peroxides.

Delépine and Horeau²⁰ studied the C.R. of various aldehydes (formaldehyde, butyl aldehyde, benzaldehyde) and aldoses (galactose, glucose, arabinose) in the presence of weak alkali and heterogenous catalysts (*e.g.* Pt, Pd, Raney-Ni). If, for instance, formaldehyde is treated in alkaline solution with Pt, hydrogen gas is formed.

¹⁴ Loew, *Ber.*, 1887, **20**, 144.

¹⁵ Müller, *Ann. Chem.*, 1920, **420**, 241.

¹⁶ Geisow, *Ber.*, 1904, **37**, 515; Lyford, *J. Amer. Chem. Soc.*, 1907, **29**, 1227.

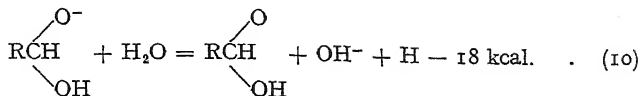
¹⁷ *Unpublished experiments.*

¹⁸ Kharasch, *J. Amer. Chem. Soc.*, 1935, **57**, 1510.

¹⁹ Urushibara and Takebayashi, *Bull. Chem. Soc., Japan*, 1937, **12**, 328.

²⁰ Delépine and Horeau, *Bull. Soc. chim. France*, 1937 (5), **4**, 1524.

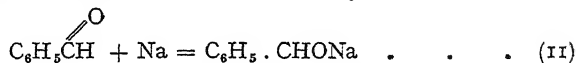
The reaction between aldehyde ions and water giving hydrogen atoms is endothermic :—



This is calculated from the heat of dissociation of H_2O (115 kcal.) (electron affinity + heat of hydration of OH^-) 150 kcal. and (electron affinity + heat of hydration) of the aldehyde ion = 53 kcal., as derived above. The actual process is probably much more endothermic, because probably only a part of the hydration energy of the OH^- ion will be gained during the electron transfer (Franck-Condon principle). Therefore, under normal conditions no decomposition of water takes place. In the presence of Pt or other metals which can adsorb the H atoms, however, the hydrogen atoms are formed on the metal surface, and we gain the considerable heats of adsorption (2.5e v./g. atom of H atoms²¹ in the case of Pt), which makes the otherwise endothermic process considerably exothermic. The adsorbed H atoms can combine on the surface to give molecular hydrogen. Whether the hydrogen is liberated as gas or is used in a subsequent hydrogenation depends largely on the metal catalyst present.

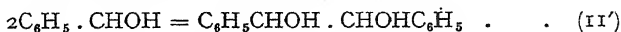
In the presence of a good hydrogenation catalyst (*e.g.* Raney-Ni) the Cannizzaro reaction occurs, whereas in the presence of a poor hydrogenation catalyst hydrogen is evolved.²⁰ Moreover, if a substance is added which is easily hydrogenated (*e.g.* crotonic acid, cinnamic acid), then instead of the second stage of the C.R. (reduction of the aldehyde) occurring the added substances are reduced (*e.g.* to butyric acid, hydrocinnamic acid).²⁰

It is seen from the above mechanism that the RCHOH radical not only acts as an intermediate, but is also capable of starting the C.R. This is proved by the following facts: When Na-amalgam is allowed to react with benzaldehyde²² (in the absence of oxygen) Na-benzoate and benzylbenzoate are obtained after decomposition with water. The addition of Na to the aldehyde results in the formation of a ketyl radical :—

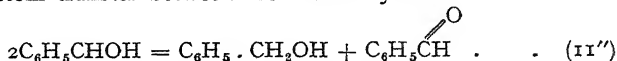


which is decomposed by water to give the $\text{C}_6\text{H}_5 \cdot \text{CHOH}$ radical.

After decomposition with water of the products of reaction of Mg-amalgam on benzaldehyde,²³ are found Mg-benzoate, benzylbenzoate and hydrobenzoin. This is formed according to the reaction :—



Hydrogen atom transfer between the radicals yields :—



In the absence of excess benzaldehyde (*i.e.* if dilute solutions of the aldehyde in ether or benzene are treated with Na) the C.R. does not occur to any appreciable extent, and we get mainly hydrobenzoin.²⁴

(d) The Cannizzaro Reaction in Heavy Water.

Bonhoeffer and Fredenhagen²⁵ found that in the reaction of "light" formaldehyde and benzaldehyde in heavy water, none of the hydrogens directly bound to the carbon underwent exchange. This is in agreement

²¹ Lennard-Jones, *Trans. Faraday Soc.*, 1932, 28, 341.

²² Alexejeff, *Ann. Chem.*, 1865, 129, 348.

²³ Kling and Roy, *Compt. rend.*, 1907, 144, 1113.

²⁴ Beckmann and Paul, *Ann. Chem.*, 1891, 266, 25.

²⁵ Bonhoeffer and Fredenhagen, *Z. physik. Chem. A.*, 1938, 138, 379.

with the proposed mechanism because the reduction of the RCHOH is brought about by the hydrogen of another RCHO molecule (reaction 5), and otherwise there is no possibility of a D atom becoming attached to a carbon atom.²⁶ Generally, the mean lifetime of the radicals is extremely short (their stationary concentration is very small) so that little opportunity is provided for exchange reactions.

2. The Action of Alcoholates on Aldehydes.

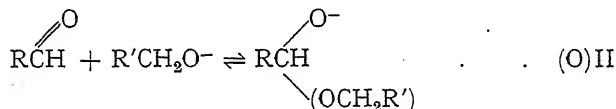
Meerwein²⁷ has suggested that the two different groups of alcoholates promote two different types of reaction.

(1) The heteropolar (ionic) alcoholates which are dissociated into ions (e.g. Na, K, alcoholates) give a sort of Cannizzaro reaction (ester formation).

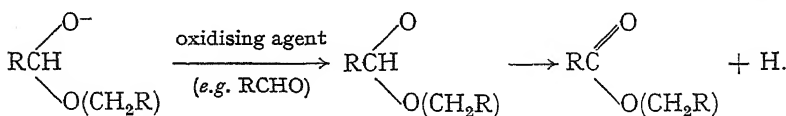
(2) The more homopolar alcoholates of Al, Sn, Zr (Mg) promote a reduction process which consists in the reduction of the aldehyde (RCHO) and oxidation of the alcoholate ($\text{R}'\text{CH}_2\text{OH}$), according to the equilibrium: $\text{RCHO} + \text{R}'\text{CH}_2\text{OH} \rightleftharpoons \text{RCH}_2\text{OH} + \text{R}'\text{CHO}$.

(a) Ester Formation (Claisen,²⁸ Titschenko²⁹).

The action of alcoholate ion is similar to that of OH^- ion in the C.R. The equilibrium corresponding to process (O)I is:



and this is followed by a set of reactions similar to (1) to (7). Eventually the RCH_2OH is formed in a reaction corresponding to reaction 5. This gives then the RCH_2O^- ion which again takes part in a reaction corresponding to equilibrium (O)II, yielding $\text{RCH}(\text{OCH}_2\text{R})\text{O}^-$ ion, which finally leads to the formation of the ester ($\text{R} \cdot \text{COOCH}_2\text{R}$) in a reaction corresponding to reaction 2; one has the following sequence of steps



(b) Reduction Process (Meerwein-Schmidt,²⁷ Ponndorf,³⁰ Verley³¹).

In alcoholates which are more homopolar in character, no appreciable amount of the alcoholate ion is present, and the molecule reacts as a whole, giving first of all a molecular compound with the aldehyde.*

²⁶ Clusius, *Ber.*, 1937, 70, 819; Erlenmayer and Schoenauer, *Helv. chim. Act.*, 1937, 20, 222.

²⁷ Meerwein, *J. prakt. Chem.*, 1936, 147, 211; Meerwein and Schmidt, *Ann. Chem.*, 1925, 444, 221.

²⁸ Claisen, *Ber.*, 1887, 20, 646.

²⁹ Titschenko, *Chem. Zentralblatt*, 1906, II, 1309, 1552.

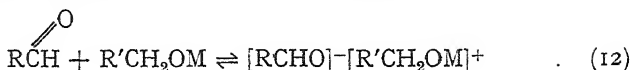
³⁰ Ponndorf, *Z. angew. Chem.*, 1926, 39, 138.

³¹ Verley, *Bull. Soc. chim.*, 1925, 37, 537, 871; 1927, 41, 1788.

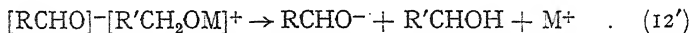
* These molecular compounds are often deeply coloured (e.g. $\text{Mg}(\text{OC}_2\text{H}_5)_2\text{Cl}$ and cinnamic aldehyde).²⁷ It has been shown elsewhere³² that the formation of coloured molecular compounds involves the formation of an ionic molecule resulting through electron transfer from the donor (alcoholate) to the acceptor (aldehyde).

³² Weiss, *Nature*, 1941, 147, 512.

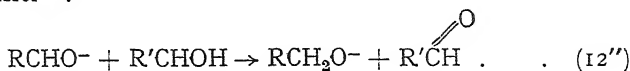
The reaction is represented by (M = monovalent metal) :—



followed by :—



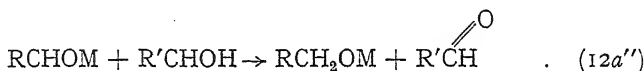
finally giving the end product (RCH_2O^- or RCH_2OH) through the hydrogen transfer* :—



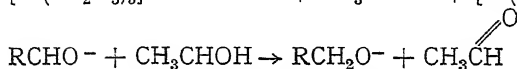
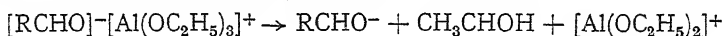
Or else we may get the undissociated radical :



followed by :—



If this is applied to the action of aluminium ethylate as the reducing agent we obtain the following sequence of reactions :—

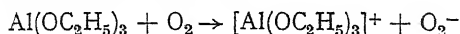


or we may get directly the $\text{RCH}_2\text{O}[\text{Al}(\text{OC}_2\text{H}_5)_2]$ instead of the corresponding ions.

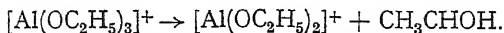
In the case of a ketone the reactions are quite similar but RCHO is replaced by R_1COR_2 and ultimately the corresponding secondary alcohol is formed.

The occurrence of $[\text{Al}(\text{OC}_2\text{H}_5)_2]^+$ follows directly from the formation of $\text{Al}(\text{OC}_2\text{H}_5)_2\text{OH}$ in the reaction between aluminium ethylate and molecular oxygen as the oxidising agent²⁷ (instead of an aldehyde or ketone).

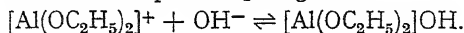
The first step is here the reaction :—



followed by :—



The CH_3CHOH is oxidised further to acetaldehyde whereas the positive ion combines with the OH^- present giving :—



3. The Action of Cyanides on Benzaldehyde (Benzoin-synthesis).

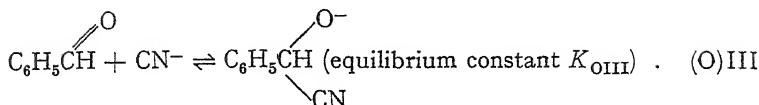
This reaction can be treated on exactly similar lines. The CN^- ion behaves similarly to the hydroxyl and alcoholate ion, as has already been assumed by previous authors.³⁵

* This is supported by theoretical considerations,³³ and by the experimental work of Bachmann on the $(\text{C}_6\text{H}_5)_2\text{COH}$ radicals.³⁴

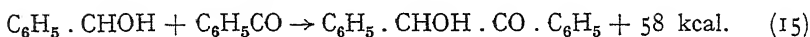
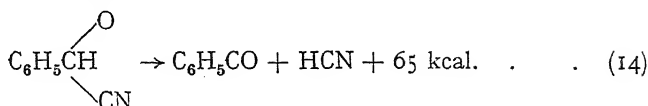
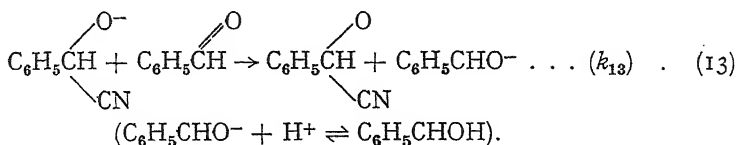
³³ Weiss, *Trans. Faraday Soc.*, 1940, **36**, 856.

³⁴ Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 355, 771.

³⁵ Stern, *Z. physik. Chem.*, 1905, **50**, 513; Lapworth, *J. Chem. Soc.*, 1903, **83**, 995.



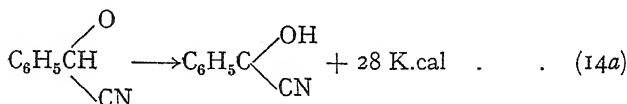
followed by :—



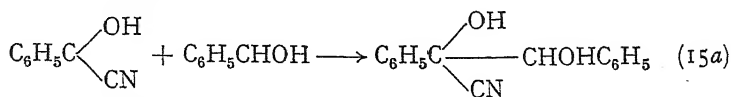
In reaction (14) we have to break one (C—C) bond (58 kcal.), and one (C—H) bond (87 kcal.), but we gain the (H—CN) bond (95 kcal.),³⁶ and the difference between the single and double carbon-oxygen bond (115 kcal.).

In the mechanism of the C.R. we have assumed mainly hydrogen transfer between the radicals (reaction 7), although combination of the radicals (reaction 15) is not excluded. Under the conditions of the benzoin synthesis, combination of the radicals is obviously the favoured process.

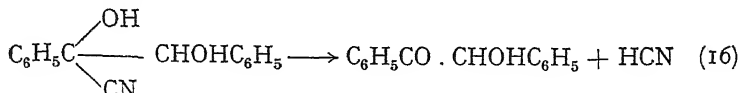
(*Added in proof.*) This is probably due to the fact that in the presence of CN^- the radical $\text{C}_6\text{H}_5\text{CO} \cdot$ will be largely present as a cyanohydrin ($\text{C}_6\text{H}_5\text{C} \begin{array}{l} \text{O}^- \\ \text{CN} \end{array}$ and $\text{C}_6\text{H}_5\text{C} \begin{array}{l} \text{OH} \\ \text{CN} \end{array}$). This may be formed by direct interaction between the radical and CN^- in a reaction analogous to process (O)III or else it may directly emerge from the process corresponding to reaction (14), viz. :—



In the case of the cyanohydrin radical combination of the radicals rather than dismutation is the favoured process and one obtains the benzoin cyanohydrin according to :—



which will eventually break up to give enzoin according to :—



³⁶ Kistiakowsky and Gershinowitz, *J. Chem. Physics*, 1933, 1, 432.

In the simplest case reaction (13) represents the slowest (time determining) step, and the rate of the benzoin formation is therefore given by the expression:—

$$\text{rate} = k_{13}[\text{C}_6\text{H}_5\text{CHO}][\text{C}_6\text{H}_5\text{CH}(\text{CN})\text{O}^-] = k_{13}K_{\text{OIII}}[\text{C}_6\text{H}_5\text{CHO}]^2[\text{CN}^-] \quad (16)$$

This is in agreement with the extensive experiments of Stern.³⁵

Summary.

(1) A mechanism of the Cannizzaro reaction has been derived which is in agreement with the experimental data available (kinetics, reaction in heavy water, etc.).

(2) This mechanism involves only simple processes (electron or hydrogen atom transfers) for which the energy requirements are fulfilled.

(3) The proposed mechanism is based on the earlier work of Haber and Willstaetter, insofar as the occurrence of the radicals RCO and RCHOH is assumed (both formed from the aldehyde RCHO through univalent oxidation or reduction respectively); some independent experimental evidence is presented.

(4) The action of alcoholate ions on aldehydes (resulting in ester formation) and of cyanide ions on benzaldehyde (benzoin—synthesis) are shown to be similar to the action of hydroxyl ions in the Cannizzaro reaction.

(5) These reactions and the reducing action of certain alcoholates on aldehydes and ketones have been discussed from a similar point of view.

My thanks are due to Professor G. R. Clemo, F.R.S., for his interest in this work.

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GENERAL DISCUSSION

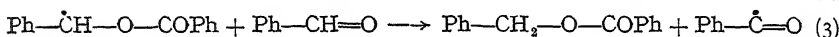
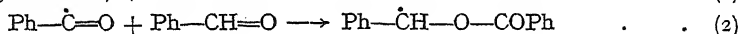
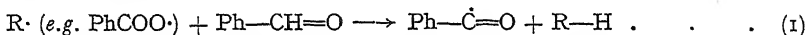
Prof. C. K. Ingold (*London-Aberystwyth*) said: In supporting his free-radical mechanism for the Cannizzaro reaction, Weiss uses arguments of two kinds. Those of the first kind may be called "permissive": they are consistent with the free radical mechanism, but they are equally consistent with mechanisms of a quite different character. To this class belong all Weiss's facts and arguments except one. That one, however, is not merely permissive: it is "compelling." It is mentioned about half-way between equations 9" and 10, and refers to the peroxide catalysis of the reaction. This, it seems to me, is the sole (but adequate) evidence that the mechanism really does involve free radicals, as Weiss maintains. The reason why I refer to the different evidential status of the two kinds of arguments adduced in relation to the Cannizzaro reaction is that Weiss suggests an extension of his mechanism to include the benzoin reaction. Here, however, I do not find any evidence of the second ("compelling") kind, and I question whether the proposed extension is justified.

Dr. C. L. Wilson (*Manchester*) said: It would not be correct to ascribe to Lapworth a process for the benzoin condensation involving radicals. Lapworth's picture was essentially two consecutive Aldol (ionic) reactions. This fits the facts better than a radical process. Radical reactions in solution are, as Waters will agree, characterised by sensitivity to specific catalysts such as peroxides, metals, or metal ions, and sometimes irradiation. A further criterion of such processes would seem to be whether or

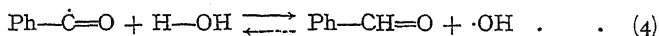
not the familiar laws of addition and substitution hold.¹ For example, peroxide catalysed addition of hydrogen bromide does not follow the Markownikov rule, the Gomberg reaction bears no relation to simple benzene substitution and the Cannizzaro process is entirely unlike Aldol addition. The benzoin condensation, however, has a strong formal resemblance to the Aldol but it will be agreed that Weiss is correct in thinking of the Cannizzaro reaction as a radical reaction, in spite of one ingenious suggestion to the contrary.²

In the reduction of the carbonyl group the superiority of a nickel over a platinum catalyst would appear to be at variance with experience. Thus, whereas a specially activated platinum can be used at ordinary temperatures and pressures, nickel requires rather drastic conditions.

Dr. W. A. Waters (*Durham*) said: The free radical mechanism for the Cannizzaro reaction is established conclusively by the proof that a peroxide catalyst is essential, but further evidence may be adduced from the fact that the condensation must have involved an addition, to the electronegative oxygen atom of the carbonyl group, by an electrophilic reagent (eqn. 2 below) and takes the opposite course to the benzoin condensation, which is a polar reaction. In accordance with the general scheme for catalysed free radical reactions³ one may write the essential reaction sequence as:—

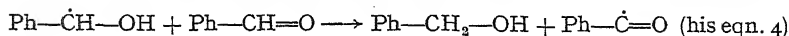
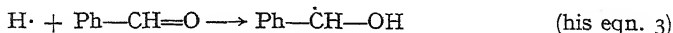
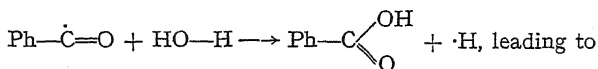


which is simpler in detail than that suggested by Weiss, and distinguishes between the initial catalysis (1) and the subsequent reaction-chain (2 and 3). Reactions 1 and 3 are just hydrogen abstractions, and for these the solvent might be an alternative hydrogen source. Under the experimental conditions normally used in the Cannizzaro reaction water molecules will undoubtedly be a possible source of hydrogen,⁵ but reactions such as 4 will not end the chain sequence, for the hydroxyl radicals thereby formed will, by the reverse reaction (indicated by the dotted arrow), regenerate organic free radicals.



The Cannizzaro reaction does in fact provide one with an excellent example of the rôle of a solvent in participating in a free radical reaction to decrease its overall rate without inhibiting the continuance of the reaction-chain.⁴

(*Communicated*): Weiss objects to my equation 4 on grounds of energetics, and I can agree that the alternative:



may be more probable in aqueous solution, and that this alternative would satisfy the conditions of no deuterium exchange with C—H links as demonstrated by Bonhoeffer.⁶

¹ Cf. Wilson, *Chem. and Ind.*, 1938, 57, 113.

² Cf. Ingold and Wilson, *Z. Elektrochem.*, 1938, 44, 95.

³ Cf. Waters, *this vol.*, p. 775.

⁴ *Ibid.*, p. 780.

⁵ Cf. Waters, *J.C.S.*, 1937, 2015.

⁶ *Z. physik. Chem., A*, 1938, 138, 379.

Arguments based on bond energies of simple compounds such as water and methane cannot safely be applied to complex molecules such as benzaldehyde in which induced polar forces and mesomeric effects both operate. Structural effects may change activation energies for bond fission by over 20 k.cal.⁷

Any suitable oxidising agent may, of course, act as the initiating radical R^{\cdot} , since oxidisers are electrophilic reagents capable both of electron abstraction (Weiss's scheme) and of proton combination (my scheme, above). The two schemes are permissible alternatives, particularly with benzaldehyde, in which the polar effects of the phenyl group and of the carbonyl ($C=O$) group combine to weaken the $C-H$ link.

Dr. J. Weiss, in reply, said: I am pleased to see that Ingold accepts the radical mechanism for the Cannizzaro reaction. Apart from the "compelling" evidence of the peroxide catalysis I think there are also the following points which give strong support to this theory.

The two stages of the reaction (a) the formation of the acid and of hydrogen atoms (which may recombine to give H_2 gas), (b) the "hydrogenation" of the aldehyde, can be separated and demonstrated by various experiments. No other theory can easily explain the intermediate formation of hydrogen atoms or the fact that the Cannizzaro reaction can be started by ketyl radicals ($RCHONa$ and $RCHOH$) as I have shown in my paper.

I agree with Ingold that at the moment there is no "compelling" evidence for the radical mechanism in the case of the benzoin synthesis. However, this is equally true for all the other mechanisms which have been proposed. The only step in the benzoin synthesis which is corroborated by experimental evidence is the initial reaction between benzaldehyde and the cyanide ions (reaction 13 in my paper) and that a subsequent reaction must take place between this addition product and another benzaldehyde molecule (which follows from the kinetics of the reaction). Nothing is really known except that.

I have assumed the radical mechanism for the benzoin synthesis in analogy to the somewhat similar Cannizzaro-reaction and because there is no experimental evidence against this. The question could be settled comparatively easily, e.g. by studying the *ortho-para*-hydrogen conversion in the reaction mixture or by the addition of suitable oxidising or reducing substances which will interfere with any radicals present thereby altering the rate of the reaction. It is hoped that it will be possible to carry out some of these experiments.

Waters has proposed quite an interesting scheme of reactions but, unfortunately, there is no experimental evidence for it and it is not capable of explaining the numerous experimental facts mentioned in my paper. Moreover some of his reactions are energetically impossible. It can be easily shown that his reaction (4) is (in the direction of the fully drawn arrow) endothermic with 28 K.cal. *viz.*, splitting of the H_2O molecule (-115 K.cal.) and formation of one $C-H$ bond ($+87$ K.cal.). Although his reaction (2) is endothermic with only 5 K.Cal. (opening of one $C=O$ bond, formation of one $C-O$ single bond), in this reaction there is made the questionable assumption of the free radical of an ester. Also one gets the impression that the Cannizzaro reaction can only be initiated by means of a ($PhCOO$) radical which is, of course, not the case as in principle OH^- ions or, alternately, every suitable oxidising or reducing agent can start the reaction:

The Cannizzaro reaction is a radical reaction but is not a chain reaction with chains of any appreciable length and, for instance, in the homogenous system no peroxides (or other catalysts) are necessary to

⁷ Cf. Waters, *J.C.S.*, 1933, 1551.

start the reaction, which is then started by reaction (1) of my paper. Only if this reaction cannot take place (e.g. heterogeneous system, very high concentration of alkali) the peroxides are necessary.

I am glad that Wilson also finds the radical mechanism acceptable for the Cannizzaro reaction.

Unfortunately, there is at present very little experimental evidence available of the kind mentioned by Wilson (sensitivity to specific catalysts, etc.) which would decide for or against a radical reaction in the case of the benzoin condensation. Actually the only reactions which are corroborated by experimental evidence are the initial reaction between benzaldehyde and the cyanide ion and the subsequent process between the addition product and another benzaldehyde molecule and there seems to be no direct evidence for the Lapworth mechanism beyond this point. I have assumed the radical mechanism for the benzoin synthesis by analogy with the Cannizzaro reaction and there is at least one instance where benzoin formation takes place from the radicals. Baekstroem⁸ has shown that on irradiating benzaldehyde in the ultraviolet benzoin is formed by combination of the radicals $\text{Ph} \cdot \text{CO}$ and $\text{Ph} \cdot \text{CHOH}$.

Wilson is such an expert on the question of catalytic reductions that I am certain that his observations are essentially correct. I have based my remarks on this point on the work of Délepine and Horeau⁹ and I believe that under the conditions of their experiments their observations are correct. However, I agree that it would be of interest to have some independent confirmation on this point.

Prof. C. K. Ingold (*communicated*): Unlike Weiss, I regard the specificity of the CN^- reagent for the benzoin synthesis—the fact that no other nucleophilic anion can be substituted—as “compelling” evidence for Lapworth’s mechanism for the benzoin reaction under normal conditions. The specificity of the reagent is by far the most distinctive fact about the benzoin synthesis, and Lapworth’s mechanism is the only one which not only accommodates it, but necessitates it.

Dr. J. Weiss (*communicated*), in reply: In correcting the proofs of my paper I have already added a short paragraph on the action of the cyanide which makes it conceivable why the presence of CN^- favours benzoin formation (combination of the radicals). I agree partly with Ingold as I also find the Lapworth mechanism an attractive possibility, and I hope that future experiments will make possible a clear decision between these two mechanisms.

⁸ *Z. physik. Chem.*, B, 1934, 25, 99.

⁹ *Bull. Soc. Chim. France*, 1937 (5), 4, 1524.

THE MECHANISM AND KINETICS OF RING-CLOSURE.

By G. M. BENNETT.

Investigations in this direction have often been of a qualitative or semi-quantitative kind, and the preparation of cyclic substances has been a principal objective apart from the elucidation of the main theoretical problem. There have, in fact, been but few accurate kinetic studies, and yet a fairly clear picture has been built up. Moreover, the application of simple kinetic principles has latterly guided some very successful experimental work in the synthesis of large rings.

General Considerations.

For a precise answer to the question as to the comparative ease of ring-closure a reaction is desirable involving the simplest possible type

of substance such as $A(CH_2)_nB$, which yields the ring compound $(CH_2)_nD$ irreversibly at convenient temperatures for measurement and without side reactions. Complete data may then be obtainable, including the constants of the Arrhenius equation. Few such reactions are known, and complete freedom from side reactions for all values of n is never found, since reactions of the "polymerisation" type to give $[(CH_2)_nD]_p$ or $A[(CH_2)_nD]_q(CH_2)_nB$ are always liable to intervene when n is more than 7.

Much information has been accumulated as to the yields of cyclic substances obtained under various conditions from open chain compounds, and these provide semi-quantitative indications of ease of ring-closure. Such comparisons will be most significant when the ring-closure reaction in two cases compared competes with some side reaction which remains essentially the same in the two cases. It should be noted that the direct comparison of percentage yield x is a fair criterion provided the yield is not high. If, for example, two yields compared are 90 and 95 % the proportion of substance following the side-reactions is halved in the latter case, and it is evident that a better comparison will be got using the value $x/100-x$ in place of x (that is, the ratio of the material going in the desired direction to that going in other directions).

To deal with the first order ring closure reaction (speed k_1c) accompanied by the second order polymeric process (speed k_2c^2) Stoll and Rouvé¹ use the quotient of these speeds $Y = \frac{k_1}{k_2} \frac{1}{c}$ which they term

"degree of ring-closure." The ratio $\frac{k_1}{k_2} = C = cY$ is their "ring-closure constant." This is of the dimensions of a concentration, and gives that value of the concentration for which $Y = 1$. It depends on solvent, temperature and substance, but should be a suitable criterion of comparative tendency to ring-closure.

Rings of 3-7 Members.

The experience of chemists with many reactions has shown the great ease of formation of rings having five, six and three members. One of the few deliberate studies of the ease of ring closure in small all-carbon rings was based on the examination of the yields of cyclic products in the action of methyl alcoholic potassium hydroxide on α -brominated dicarboxylic esters.² The results were complicated by a variety of side-reactions, by the subsequent disruption of the three-membered ring, and by steric factors of the kind discussed by Bischoff, yet they clearly demonstrated the easy formation of three- and five-membered rings and the difficulty in producing the four- and most of all the seven-membered rings, and similar comparisons were also used to study the operation of the Thorpe-Ingold valency deflexion effects.

An accurate study of the formation of heterocyclic rings with one nitrogen atom as member was made by Freundlich and his collaborators from 1911 onwards.³ The reaction $Br(CH_2)_nNH_2 \rightarrow (CH_2)_nNH + HBr$ was found to be of the first order in presence of alkali in water or aqueous alcohols. It is irreversible and unaffected by catalysts. The results

¹ *Helv. Chim. Acta*, 1934, 17, 1289.

² Ingold and others, *J.C.S.*, 1921, 119, 305, 951, 2001; 1926, 1465, 1471.

³ *Z. physik. Chem.*, 1911, 76, 79; 1912, 79, 681; 1914, 87, 69; 1926, 122, 39; *A.*, 1933, 166, 161.

for 3-7 membered rings are shown in Fig. 1 and the constants of the Arrhenius equation in Table I.

Another reaction which has served for similar comparisons is the formation of cyclic sulphonium salts from ω -halogenated sulphides:

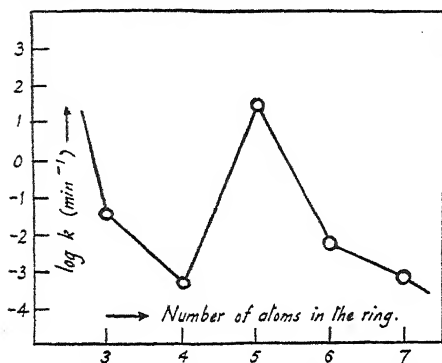
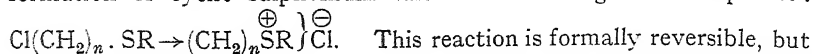


FIG. 1.—Comparison of velocities of ring-closure for the series $\text{Br}(\text{CH}_2)_n \cdot \text{NH}_2$ in aqueous solution.

for 5, 6 and 7 membered rings in 50 % acetone-water the reaction is found to be of the first order and practically complete. Examination of the smaller rings by this reaction is, however, excluded by the pronounced reversal of the reaction. Comparisons were made⁴ of the closure of the five- and six-membered rings with $\text{R} = \text{C}_6\text{H}_5$, and of the six- and seven-membered rings with $\text{R} = \text{C}_2\text{H}_5$, and combining these results we have relative velocities

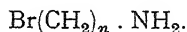
$$5 : 6 : 7\text{-rings} = 6000 : 76 : 1.$$

The ease of closure of various rings therefore falls by two or three powers of ten as the size of ring passes from five to six and again from six to seven members. The activation energies in the sulphur ring closures are of the order 20-24 K.Cal.

No. of atoms in ring	3	4	5	6	7
Activation Energy, E, K.Cals	24.9	23.2	c. 16.8	c. 18.3	24.9
Log. Z sec. ⁻¹	14.8	11.4	c. 12	c. 11	13.3

The data available do not at present justify any attempt to assess the effects of the nature and the size of the hetero-atom on the ease of ring-closure.

The influence of the solvent and its explanation has been discussed in detail by Salomon.⁵ The ring-closures have a speed in toluene or xylene which is of the order 100 times smaller than in water. The activation energy is, in fact, 4 K.Cal. (6-ring) or 10 K.Cal. (7-ring) lower in xylene, but the factor Z is also very much smaller (6-ring 10^{11} in water, 10^5 in xylene; 7-ring 10^{13} in water, 10^4 in xylene), so that the relative speeds of closure of the two rings in two different solvents, although similar, are the result of different factors. The seven-membered ring is formed more slowly than the six-membered in water, mainly as a result of the higher activation energy necessary, whereas the relative slowness in xylene as compared with the six-membered ring-closure is principally due to the less favourable Z value. The large difference in Z in different solvents is interpreted by Salomon as due to their effect on the average disposition of the parts of the reacting molecule



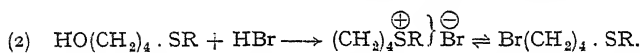
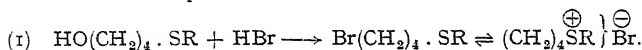
⁴ Bennett and others, *J.C.S.*, 1929, 2567; 1938, 813.

⁵ *Trans. Faraday Soc.*, 1936, 32, 153.

The molecule is regarded as existing in an equilibrium between open and coiled shapes: chain position \rightleftharpoons ring position, and this is influenced to the right hand by the solvent water but not by xylene, since the long chain will tend to adopt a shape which offers the least surface of contact with the solvent of high polarity.

Mechanism of Direct Formation of Cyclic Sulphonium Salts from Hydroxysulphides.

Experiments on the velocity of the reaction between hydrobromic acid and ω -hydroxysulphides of varying chain-length⁶ revealed an extremely high velocity of reaction when the hydroxyl group was separated from the sulphur atom by four atoms in the chain, that is for sulphides of the structure $\text{HO}(\text{CH}_2)_4\text{SR}$, and it became evident that the abnormal reactivity depended on the great ease with which the sulphur atom and the $\cdot\text{CH}_2\text{OH}$ group could approach each other. The product of the reaction was found to be chiefly the cyclic sulphonium salt $(\text{CH}_2)_4\text{SR}^+\text{Br}^-$, but ring closure of the hydroxysulphide in the absence of acid certainly does not take place. There appear to be two possible mechanisms for this process as shown below:—



The occurrence of halogenated sulphide in the products of such a reaction had been demonstrated, but this was not conclusive for mechanism (1) since the sulphonium salt formation is a reversible reaction, and so might give rise to the open chain bromosulphide also by mechanism (2). Recently a decision has been made between these two possibilities by comparing the speed of reaction of such a hydroxysulphide with hydrochloric and hydrobromic acids under similar conditions. According to scheme (1) the process should be slower with hydrochloric acid at each stage, since alcohols react more slowly with hydrochloric than with hydrobromic acid, and since alkyl chlorides add to sulphides more slowly than do alkyl bromides. If mechanism (2) is correct, however, the reaction will involve hydrogen ions and provided that the hydrogen ion activity is similar for the two acids, the rate of disappearance of acid should be the same for hydrochloric and hydrobromic acids. This is found to be the case so that mechanism (2) is confirmed.

Large Rings.

The discovery that the naturally occurring substances civetone and muscone contained large rings led Ruzicka in 1926 to examine the preparation of cyclic ketones by the thermal decomposition of the metal salts of dicarboxylic acids with extended chains.⁷ The thorium and yttrium salts were found to give comparatively good yields of the larger ring ketones (although the calcium salt is better for producing *cyclopentanone*). The appearance of small but definite yields of ring ketones with up to 18 members and diketones up to 30 members and the complete stability of these large ring structures was explained by the Sachse-Mohr

⁶ Bennett and Mosses, *J.C.S.*, 1930, 2364; 1931, 2956.

⁷ *Helv. Chim. Acta*, 1926, 9, 249, 339 and later.

theory of strainless non-planar rings. The general trend of ease of ring formation was accounted for by Ruzicka's well-known conception of the diminishing probability of the ends of the chain meeting as it increases in length, modified for short chains by the strain factor which opposes the closure of four- and three-membered rings.

Since that time considerable progress has been made in the study of various types of large ring by the application of kinetic principles. The ring-closure reaction must always be in competition with the corresponding intermolecular reaction of the second order. Since the latter depends on the concentration while the first order process does not, the ring-closure is favoured when the reaction is carried out at high dilution. This point had been emphasised and used by Ruggli as far back as 1912,⁸ but the type of ring studied was an unusual one, including an acetylene bond and the work attracted little attention.

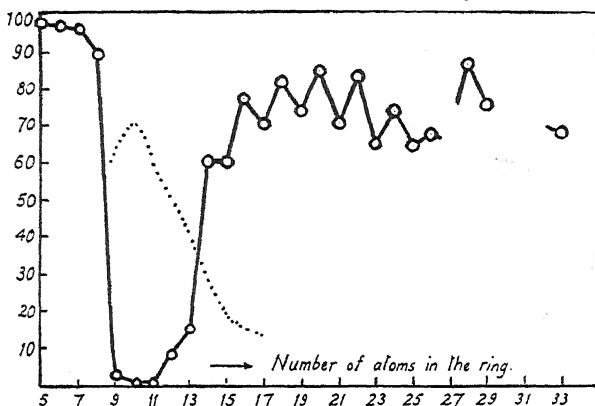
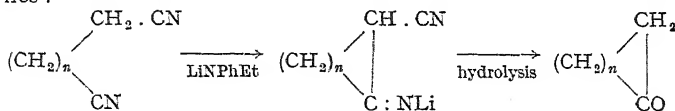


FIG. 2.—Yields per cent. of cyclic ketones in the Thorpe reaction.

○—○ monomeric ketone.
 dimeric diketone.

The researches of Ziegler and his colleagues (1933-1937)⁹ have been based on this principle, and are important because a suitable reaction was found involving smooth carbon-ring-closure; the extent of dilution necessary for success was demonstrated, and a simple practical method was used which gives high dilution without the necessity of unwieldy volumes. The material was introduced over a long period (days or weeks) into a moderate volume of solvent containing the reagent. The reaction in question is the Thorpe imino-reaction as applied to dinitriles:—



the reagent being the ether-soluble lithium derivative of ethylaniline. The product separates as the lithium compound insoluble in the ether used as solvent, the reaction thus becoming practically irreversible.

⁸ *Annalen*, 1912, 392, 92 and later.

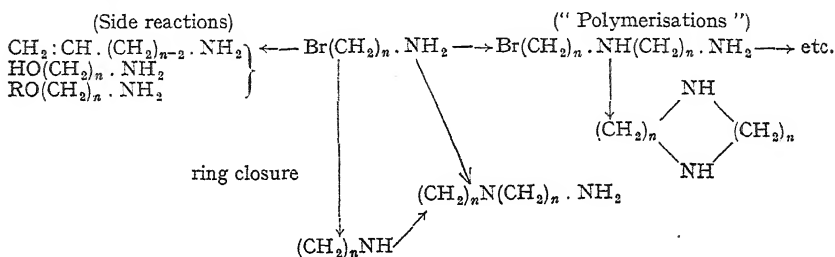
⁹ *Ibid.*, 1933, 504, 94; 1934, 513, 43; 1937, 528, 114.

The results obtained are shown in Fig. 2 where the yield of cyclic ketone is plotted against chain length.

Kinetic Analysis for Larger Rings.

After Ziegler's first successful application of the dilution principle Salomon¹⁰ undertook a close examination of the ring-closure reactions in the series $\text{Br}(\text{CH}_2)_n\text{NH}_2$ producing rings of 10, 12, 14, 15, and 17 members, which serves to provide a more quantitative scale for the comparisons of the extreme velocities of ring-closure in this range.

The main reactions which arise are given below:—



The progress of the reactions is followed by titration of the bromion liberated. The main first order reaction is accompanied by a number of second order processes leading to "polymeric" substances, some of which contain halogen and some are true polymerides. At the same time there are side reactions, of which hydrolysis is the most important, and may be of second order involving hydroxyl ions, or of the first order in a reaction with the solvent. By observing the reaction at successively higher dilutions until the result is independent of further dilution the processes of second order are eliminated (including some secondary reactions between the amines and bromo-compounds which will show an apparent first order owing to the excess of amines present). Hydrolysis dependent on hydroxyl ion concentration can be directly diagnosed by varying the latter, but it is evident that side-reactions which are independent of concentration cannot be detected kinetically, and guidance is here obtained by preparative experiments and examination of the relative yields of various products. The concentration in aqueous alcoholic solution at which reactions of higher order were absent was 0.005 molar for the 14-membered ring-closure and 0.0005 molar for the 12-membered ring. The corresponding figure for the 5- or 6-ring reactions would be the imaginary figure of 10 mols./litre.

In this way exact or approximate figures of relative velocities of ring closure were obtained which are as follows:—

Number of atoms in ring	5	7	10	12	14	17
Comparative velocity of ring closure	$4 \cdot 10^{10}$	10^7	1	$5 \cdot 10^2$	10^4	$2 \cdot 10^4$

These figures clearly follow the shape of Fig. 2 as far as the 17-atom ring, but they also give a measure of the extreme variations from maximum to minimum.

¹⁰ *Helv. Chim. Acta*, 1936, 19, 743; also reference 5.

Lactones with Large Rings.

The formation of large ring lactones from the ω -hydroxy acids by direct ring closure has been studied by Stoll and Rouvé¹¹ working at high dilution in boiling benzene with benzenesulphonic acid as catalyst. Water was removed progressively during the reaction, the reversal of which was thus largely prevented. In this way the 16- and 17-membered rings were obtained in yields of 87 and 94 %. Approximate velocities

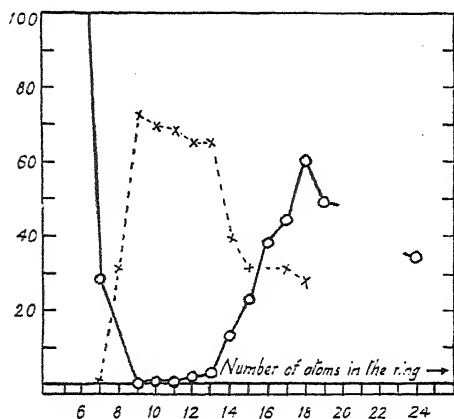


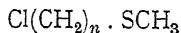
FIG. 3.—Comparative tendencies to ring-closure for the lactones.

○—○— "Ring-closure constants" for simple rings in 10^{-4} mol./litre.
 ---x--- Yields per cent. of dimeric ring.

of reaction were measured in some cases, but the conclusions are based mainly on a set of comparative yields. The results (Fig. 3) clearly display the same features as those of Ziegler.

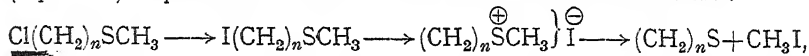
Large Ring Sulphides.

In an examination of the chlorosulphides



with n from 7 to 18 velocity measurements were not made, but the possibility of isolating large ring compounds was confirmed.¹² High temperatures and a polar solvent were necessary, but hydroxylic solvents were excluded, as they caused rapid alcoholysis. The chloro-

sulphide was heated in highly dilute solution in boiling acetophenone (b.p. 202°) in presence of sodium iodide when the reactions were:—



accompanied to some extent by "polymeric" processes. No monomeric ring-product was detected when the ring size would have been 8-13 members, but the sulphides with 15, 17 and 19 atom rings were isolated and characterised.

Large Rings attached to the Benzene Nucleus.

The familiar ease of closure of 5- and 6-membered rings between o -substituents is readily understood, in view of the fixed positions of 4 of the atoms concerned. A recent study of ring formation in the series of bromoalkyl catechol ethers $o\text{-C}_6\text{H}_4$ $\begin{matrix} \text{O}(\text{CH}_2)_n\text{Br} \\ \text{OH} \end{matrix}$ concerns rings up to 14 members.¹³ The cyclic ethers were formed in alcoholic sodium ethoxide solution and velocities of reaction were determined showing the following relations in the series:—

¹¹ *Helv. Chim. Acta*, 1934, 17, 1283; 1935, 18, 1087. See also Davies, *Trans. Faraday Soc.*, 1938, 34, 410.

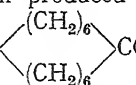
¹² Bennett and Gudgeon, *J.C.S.*, 1938, 1891.

¹³ Ziegler and Lüttringhaus, *Annalen*, 1937, 528, 162, 181.

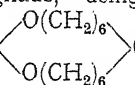
Number of atoms in the ring (= $n + 4$)	6	7	8	9	10	11	12 13 14
Comparative velocity of closure	5×10^4	370	22	5	2	1	c. 1 to 0.5

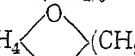
There is here no sign of the extreme minimum found in the simple alicyclic series, but it must be noted that this result is at least in part due to the presence of two oxygen atoms in the chain (see below, under "Steric Effects").

Large rings bridging the *meta*- and *para*-positions of the benzene nucleus have recently been produced by several workers. Ruzicka

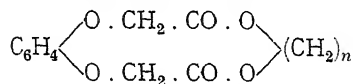
isolated the ketone *m*-C₆H₄  CO, but could not detect the for-

mation of its *p*-isomeride. Ziegler and Lüttringhaus,¹⁴ using the method

of high dilution, prepared both *m*- and *p*-C₆H₄  CO from the

dinitriles in yields of 50 %. Bridge ethers C₆H₄  (CH₂)_n were also

isolated, *m*- with $n = 7$ and 10, *p*- with $n = 8$ and 10; and 1:5- and 2:6-dihydroxynaphthalenes were successfully bridged with a chain of 10 methylene groups. Similarly, Carothers, by the depolymerisation method (see below) prepared esters of the formula



with $n = 2, 3, 4, 6, 9$ and 10 for the *meta* configuration and $n = 4, 6$ and 10 for the *para*.

Steric Factors in the Formation of Large Rings.

The most striking points which require explanation are the minimum in ease of ring-formation for rings of 9, 10 and 11 atoms (always accompanied by a strong tendency to the formation of dimeric rings), and the marked alternation between odd- and even-numbered rings apparent in both Figs. 2 and 3. The latter feature is also shown in the work of Carothers, from which it is evident that the odd-membered rings are less stable.

The minimum ease in ring formation was correlated by Ruzicka and Stoll with a maximum in the density curve for the series of cyclic hydrocarbons and ketones and a depression in their molecular refractivities.¹⁵ Models show that as the number of atoms in the ring rises beyond 6 the methylene groups are, some of them, forced to turn their hydrogen atoms inwards, and this leads to a congestion in the middle which is not completely relieved until the 15-atom ring. All the larger rings have space for the free vibration of the methylene groups, and can be formed by two zig-zag chains running parallel and connected at the ends by two loops. The congestion in the 10-atom ring must constitute a compression acting against the continuous thermal movements in the chain,

¹⁴ *Annalen*, 1934, 511, 1.

¹⁵ *Helv. Chim. Acta*, 1930, 13, 1152.

but the effect on the heat of combustion is not very marked. The figure for cyclododecane has been given as 157.6 K.Cal. per methylene group,¹⁶ as compared with 157 K.Cal. for open-chain hydrocarbons, and 156-157 K.Cal. for larger rings. The probability of a chain attaining a coiled arrangement which is almost closely packed must, however, be extremely small, owing to frequent internal collisions. This view is supported by the fact, demonstrated repeatedly, that the introduction of oxygen atoms into the chain diminishes the difficulty of ring closure. The dinitrile $\text{O}[(\text{CH}_2)_4 \cdot \text{CN}]_2$, for example, gave a 5 % yield of cyclic ketone the 10-membered ring of which contains one oxygen atom, and $[\text{—CH}_2 \cdot \text{O}(\text{CH}_2)_4 \cdot \text{CN}]_2$ a 70 % yield of the 13-membered ring with two oxygen atoms.¹⁷

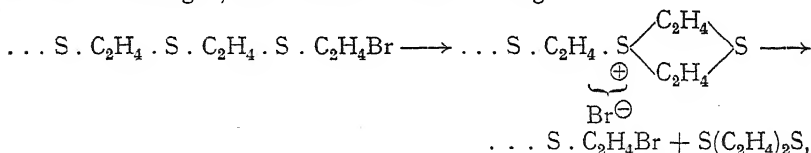
The simplicity of the arrangement of an even-numbered zig-zag chain looped into a large ring is upset by an addition of one methylene group. This must involve the introduction of an irregularity, the ring becoming appreciably less probable, and this shows itself in the alternations for odd- and even-numbered rings.

A surprising feature of Ziegler's curve is the shallow minimum at the 25-membered ring followed by a maximum at 28. The author is convinced that this phenomenon is real, but it remains unexplained.

Ring Formation by Depolymerisation.

This constitutes an entirely distinct method of approach to cyclic substances, and may have distinct advantages. It is applicable where the main ring-closure reaction is definitely reversible, as, for example, with esters, lactones, anhydrides and sulphonium salts.

One of the earliest instances was the formation of dithian (diethylenedisulphide). The action of alcoholic potassium sulphide on ethylene dihalides yields mainly polymeric ethylene sulphides, some specimens of which give dithian by dry distillation or heating with a solvent.¹⁸ It was shown¹⁹ that the depolymerisation requires the presence of a small amount of halogen, the essential reaction being:—



which can be repeated indefinitely, and depends on the reversibility of sulphonium salt formation.

Recently Carothers has applied depolymerisation methods²⁰ to the isolation of many cyclic lactones; esters and anhydrides.

The polymeric material is heated (200-300°) under low pressure (sometimes in a molecular still) usually with the addition of a catalyst such as potassium carbonate or magnesium chloride, when monomeric and dimeric products escape and are condensed. In the series of anhydrides of the acids $(\text{CH}_2)_n(\text{COOH})_2$ unstable monomeric rings of 7, 8, 10, 12, 14 and 15 members were obtained, dimeric solid anhydrides

¹⁶ Hückel, Gercke and Gross, *Ber.*, 1933, 66, 563.

¹⁷ Ziegler and Holl, *Annalen*, 1937, 528, 143.

¹⁸ Crafts, *ibid.*, 1863, 128, 220; V. Meyer, *Ber.*, 1886, 19, 3262.

¹⁹ Bell, Bennett and Hock, *J.C.S.*, 1927, 1803.

²⁰ *J. Amer. Chem. Soc.*, 1932, 54, 1557; 1933, 55, 5023; 1936, 58, 654.

replacing those of 9, 11 and 13 members. Similar results were observed with polyesters such as those from the glycols with dibasic acids. Good yields of large-ring lactones were obtained on a larger scale and in a much shorter time than in Stoll and Rouvé's experiments. The yield of monomeric 11-membered ring was 12 %, with 70 % of dimer, whereas for the 15-membered ring the figures were 90 % of monomer and 6 % of dimer.

It was a surprising fact that Ruzicka should have obtained considerable yields of large ring ketones working with solid or liquid material, even though the high temperatures should favour the ring-closure reaction. Carothers demonstrated that the thorium salt of hexadecanedicarboxylic acid yields on heating a long chain polyketone acid of the type $\text{HOOC}[(\text{CH}_2)_{16} \cdot \text{CO}]_n \cdot \text{OH}$. Heated in the molecular still at 300° this yielded *cycloheptadecanone* by a depolymerisation process, and the suggestion was made that this constitutes the mechanism of Ruzicka's preparations. The ring ketone was, however, only detected by its (very characteristic) smell in this experiment of Carothers, and the suggestion²¹ that the polyvalent thorium ion brings the ends of the chains together, is a more satisfactory alternative explanation.

*King's College (London),
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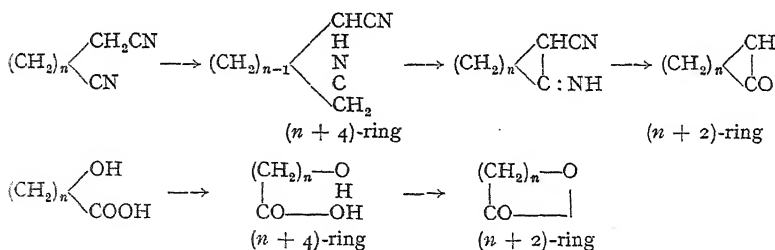
²¹ Mills, *Solvay Reports*, 1931, p. 21; also *Helv. Chim. Acta*, 1928, 11, 670.

GENERAL DISCUSSION

Prof. C. K. Ingold (*London-Aberystwyth*) (*Communicated*): The difficulty of closing a four-membered ring (*cf.* Fig. 1) may be connected with the circumstance that this is the smallest ring containing atoms not directly linked to each other. In consequence there may be a maximum of interatomic repulsion in the normal state, and in the activated states of formative processes.

Dr. G. N. Copley (*Liverpool*) (*Communicated*): The marked alternation between the odd- and even-membered rings shown in Figs. 2 and 3 suggests the following remarks.

Assume that Thorpe's dinitrile reaction and the lactonisation of ω -hydroxyacids proceed *via* a hydrogen bridge in the transition state:—

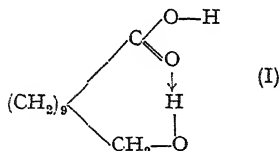


To produce an even-membered ring an even-membered ring is involved in the transition state, and to produce an odd-membered ring an odd-membered ring is involved in the transition state, in both reactions. Hence it might be expected that there should be a correlation between the rates and equilibria for these reactions.

The hydrogen bridge can actually tend to form twice inside the same dinitrile or ω -hydroxyacid molecule. Now the groupings $\begin{array}{c} \text{H} \\ | \\ \text{O} \text{---} \text{H} \text{---} \text{C} \end{array}$ (I) and $\text{---} \text{C} \equiv \text{N} \text{---} \text{H} \text{---} \text{C} \text{---}$ (II) are linear when strainless, so that rings containing these groupings will not tend to form very readily until there are about four (for I) and seven (for II) additional carbon atoms closing the ring. This is deduced from models. Hence this alternative chelation will begin to come into action and prevent the larger rings forming at approximately the 10-ring in the case of lactones and the 14-ring in the case of cyclic ketones. In the formation of still larger rings of these two kinds there are many alternative types of chelation possible and the rapid chelations which led to the beginnings of the production of 6-ring lactones and 8-ring ketones no longer monopolise the reaction and large rings are formed with greater ease again.

Alternation stands out much more markedly in the Thorpe reaction than in the formation of lactones. This difference may be attributed to the fact that the Thorpe reaction uses a molecule in which the terminal co-ordinating groups are the same, whereas in the ω -hydroxyacids they are not. It appears, therefore, that alternation is connected with "double chelation" also, being more marked in the Thorpe reaction because both co-ordinating groups are equally effective.

Dr. M. M. Davies (*Communicated*): A careful study of both the catalysed and uncatalysed condensation of omega-hydroxyundecanoic acid $[\text{CH}_2\text{OH} \cdot (\text{CH}_2)_9 \cdot \text{COOH}]$ in different solvents has related the nature of the reaction product to the molecular state of the reactant.¹ The reaction product consists of the dilactone or the open-chain polyester according to the degree of association of the reactant: when this is monomeric the lactone is produced, whilst association of the reactant, which is very pronounced in non-polar solvents, results in the formation of the polyester. In the interpretation of the data it was indicated that the monomeric hydroxyacid molecule in solution might assume a ring configuration (I) whose form could easily lead to the lactone. Similarly,



head-to-tail association which was suggested by the molecular weight results in concentrated solutions, predisposed the molecules to polycondensation.

A subsequent infra-red study of the reactant hydroxyacid in carbon tetrachloride substantiated at each stage the picture of the behaviour of this solute arrived at by the more indirect indications of the kinetic analysis.² In particular, confirmation was forthcoming of the occurrence of a cyclic form of the monomeric molecules in solution.

Finally, it may be emphasised that inter- and intramolecular association may well play an important part in determining the kinetic details of a reaction in organic solvents. For an esterification reaction in benzene the results are consistent with the view that only the monomeric molecules of the reactants are kinetically active.³

¹ *Trans. Faraday Soc.*, 1938, **34**, 410.

² *J. Chem. Physics*, 1938, **6**, 770.

³ *Trans. Faraday Soc.*, 1937, **33**, 331.

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